INSTITUTION OF GAS ENGINEERS.

AUTUMN MEETING AT THE INSTITUTION OF ELECTRICAL ENGINEERS IN LONDON, NOV. 13 and 14.

The President, Mr. Charles S. Shapley, in the Chair.

SECOND REPORT OF THE AMMONIA SUB-COMMITTEE.

(*Continued from p. 42.*)

THE ZINC PROCESS FOR THE EXTRACTION OF AMMONIA AND SULPHURETTED HYDROGEN FROM GAS.

By PROFESSOR J. W. COBB, C.B.E.

This process was worked out in the laboratories of the Farnley Iron Company, primarily for the purpose of utilizing the sulphur contained in the coal gasified in a Mond bye-product producer gas plant for the purpose of making ammonium sulphate, so dispensing with the necessity for supplying sulphuric acid from outside. It had the advantage compared with somewhat similar processes proposed for the same purpose of being one which would be worked on a gas which had not been previously freed from tar.

The first part of the process consisted in passing the gas above the dew-point through a solution of zinc sulphate maintained at a temperature between 80° and 90° C. The following reaction occurred :—

$$(NH_4)_2S + ZnSO_4 \rightarrow ZnS + (NH_4)_2SO_4,$$

that is, all the ammonia and H_2S equivalent to it were removed from the gas, the excess H_2S going forward. The solution of ammonium sulphate was filtered from the precipitate of zinc sulphide, and the ammonium sulphate recovered by evaporation in neutral solution.

The next step was the regeneration of zinc sulphate from zinc sulphide. It was not found possible to do this directly by simply roasting, but the method finally adopted was to roast the zinc sulphide with an excess of air and to pass the resulting gases through water in which the oxidized solid product from a previous roasting was suspended, when zinc sulphate was formed, as may be represented simply thus :—

$$ZnO + SO_2 + O = ZnSO_4.$$

The regenerated zinc sulphate was then used again.

On the works scale for the purpose of the first absorption from the gas, the solution of zinc sulphate was fed into the top of a Feld centrifugal washer, up which the gas was passing. The uppermost compartment of the washer could be reserved for a separate feed of zinc oxide in suspension, in order to make up any loss of sulphur in the subsequent processes, by producing an excess of zinc sulphide, thus :—

$$ZnO + H_2S = ZnS + H_2O.$$

The precipitation and control of the washer offered no difficulty, and the zinc sulphide precipitate was easily separable from the zinc sulphate solution by an ordinary filter press. The action of the zinc sulphate solution on the gas was extremely rapid.

The zinc sulphide precipitate was grey in colour from a little contained tarry matter, and was roasted in a simple shelf burner, the small amount of heat required to supplement that obtained from the oxidation being provided by a gas jet in each shelf.

The plant described was planned for the production of about 1 ton of sulphate of ammonia per day. It was realized that a roaster of less simple design and construction would be required for the best results on a larger working scale.

The zinc sulphide roasted easily and well, the oxide being obtained as a powder, which after sieving, was used in the next part of the plant, the absorber. This was a circular oak vat containing water to the depth of about 5 ft., into which the zinc oxide from the roaster was charged and agitated by a revolving, hollow, perforated arm. The gases from the roaster were drawn by a Roots blower, and blown down a hollow central shaft, through the perforations of the revolving arm, into the zinc oxide suspension. It was the slow working of the oxidizing process in the absorber which created the practical difficulty of the process, and no means was found of speeding it up to an extent which guaranteed commercial success. Too rapid a supply of SO_2 had to be guarded against, since that caused the formation of crystalline insoluble zinc sulphite, which was only very slowly converted into soluble zinc sulphate. The power cost for blowing the gases, mainly air with a small percentage of SO_2, through the liquid, were such as to make the economic position doubtful, unless the cost of sulphuric acid was very high. Two vat absorbers were employed, and when a sufficiently strong solution of zinc sulphate had been obtained in one absorber, the other was put into operation. The suspension in the first was allowed to settle out and the zinc sulphate run off. It was usually concentrated by steam-pipe heating before using again in the Feld washer. A little residual zinc oxide suspended in it did no harm.

SUMMARIZING.

(1) The process certainly worked in making ammonium sulphate from the sulphur in the coal, without providing sulphuric acid from outside.

(2) The slowness of the oxidation process in the absorber made the power costs for blowing heavy, and rendered economic success doubtful on that account. No means of satisfactorily speeding up the oxidation was ascertained.

(3) The succession of operations necessary, for any size of the plant, would make its labour costs too heavy, unless the process was being worked on a considerable scale. It would be unsuitable for a small plant, whether gas-works, coke-oven plant, or bye-product gas producer plant.

THE BURKHEISER PURIFICATION PROCESS.

By PHILIP G. G. MOON.

The Burkheiser purification process, invented before the European War by Herr Burkheiser, caused much interest at the time, but owing to the intervention of the war years, little has been heard of it since. The aim of the process is the extraction from the gas, from retorts or coke ovens, in the same continuous process, of sulphur, ammonia, and cyanogen, and their conversion into a valuable ammonium salt, the acid required being obtained from the sulphur impurities themselves. The impurities are removed from the gas in the reverse order from that at present in use, the sulphur being taken out first and the ammonia afterwards.

In its original form the process was a "dry" one, but owing to mechanical difficulties it has been found neces-

sary to modify it, and to make it in its final form a "wet" process.

UNDERLYING PRINCIPLES.

In the original process the gas from the retorts or coke ovens was cooled, and the tar removed in the usual way. The virgin liquor from the hydraulic main was worked up as usual, and the vapours returned to the main gas stream, so that the whole of the ammonia, sulphuretted hydrogen, and cyanogen were in the gas when it entered the purifiers.

Removal of Sulphuretted Hydrogen and Cyanogen.—The purifiers were iron boxes containing a specially prepared hydrated oxide of iron free from fibrous material, and which, while containing some combined water, was quite dry and very porous. It was obtained in grains about the size of peas from bog-ore. A gas speed of from 25 to 30 times that ordinarily employed could be maintained, owing to the activity of the oxide in absorbing sulphuretted hydrogen, and it was therefore possible to use much smaller purifiers for a given volume of gas, an important feature of the process. In these purifiers the sulphuretted hydrogen and cyanogen were removed, the former by the usual reaction forming ferric sulphide, and the latter as ammonium sulphocyanide. The heat of the reaction was sufficient to keep the water always produced by the reaction in the form of steam, so that the pores of the material were not clogged, and the purifiers were kept warm (which was accomplished by using the waste heat given off during regeneration), the oxide remained dry and porous until completely spent.

Revivification.—When fouled the material was revivified in the purifier itself by blowing a regulated current of air through the box. The ferric sulphide was oxidized in the usual manner, and the temperature rose sufficiently to cause the liberated sulphur to burn, giving sulphur dioxide. The heat was regulated by circulating water, this heated water being used to warm the working purifiers as mentioned above. The sulphur oxides were passed to a scrubber where they were used in the recovery of the ammonia.

Cyanogen Recovery.—The cyanogen could be recovered separately if desired by treating the gas before it entered the Burkheiser plant, but in most cases this would not be remunerative.

The sulphocyanides were converted during revivification into ammonia, which was recovered in the ammonia recovery plant. This caused an increase of from 8 to 10 per cent. in the yield of ammonia sulphate per ton of coal.

Ammonia Recovery.—In order to recover the ammonia as a solid salt, the oxides of sulphur obtained in the revivification of the spent oxide were used to supply the necessary acid. The gas leaving the purifiers contained all the ammonia, but no sulphuretted hydrogen or cyanogen. It was lead up through a tower fitted with wooden grids or any device giving a large surface, called the "gas scrubber," down which a solution of ammonium bisulphate and bisulphite was trickling. This solution being acid, absorbed the ammonia with avidity, forming a neutral solution of ammonium sulphate and sulphite. This solution passed to another similar tower called the "air scrubber," where it came in contact with the gases from the purifiers undergoing revivification—namely, oxides of sulphur, some nitrogen, and excess air. It was here acidified again, and a mixture of ammonium bisulphate and bisulphite formed, any excess sulphur dioxide escaping from the top of the tower. By pumping the liquor alternately through these scrubbers both ammonia and oxides of sulphur were taken up until the solution became saturated and solid sulphate and sulphite crystallized out. (Ammonium bisulphate and bisulphite never separated owing to their much greater solubility.)

For the successful working of this process the liquor must not be diluted unduly, that is, the water condensing in the scrubbers from the gas and air streams must not exceed appreciably that removed by the formation of sulphate and sulphite, as shown by the equations :—

$$2NH_3 + SO_3 + H_2O = (NH_4)_2SO_4$$
$$2NH_3 + SO_2 + H_2O = (NH_4)_2SO_3.$$

That is to say, the gas and air streams must be passed through small condensers before entering the scrubbers if necessary.

The separation of solid salt was arranged to take place in the saturator where the concentrated liquor met the gas straight from the purifiers and rich in ammonia. The concentration of the liquor was observed by taking its density with a hydrometer. Salt extraction could be carried on continuously or intermittently.

The salt formed was a mixture of ammonium sulphate and sulphite containing from 50 to 65 per cent. of sulphate, generally called Burkheiser salt, and it appeared impossible to obtain a larger percentage of sulphate. The relative proportions are determined by the physico-chemical behaviour of saturated solutions of sulphate and sulphite, the amount of oxidation occurring due to the oxygen always present in the gas, and to the temperature. With regular working of the plant the composition of the salt can be kept fairly constant.

The salt obtained was of a good colour, and contained no free acid—a great advantage in view of the damage done to bags during transport when this is present.

The colour of the salt might be impaired if a considerable quantity of ammonium thiosulphate were formed in the liquor, due to its decomposition with deposition of sulphur. This would occur through any large amount of sulphuretted hydrogen getting forward into the gas scrubber, which acts as a very efficient catch purifier. It is easily remedied by allowing the fouled liquor to stand a day or two while other liquor is used, when the thiosulphate decomposes and the deposited sulphur settles and the liquor can be decanted from it.

It has also been found that concentrated solutions of ammonium bisulphite at high temperatures decompose, forming ammonium thiosulphate, ammonium sulphate, and sulphur, and research work on this point is in progress.

The Burkheiser salt has been tested by Dr. Weiler, of Aix-la-Chapelle, and found to have no injurious effects on plant life, but to be, in fact, a rather better fertilizer than ordinary sulphate giving better results with oats, potatoes, and turnips than an equal quantity of sulphate (calculated on an ammonium basis).

If, however, there were a prejudice against the Burkheiser salt until its value became established, it can be converted at little cost into ammonium sulphate by passing the salt slowly with a current of air through a tube a portion of which is heated to about 100° C. The sulphate passes through unchanged, but the sulphite volatilizes and recombines in the cool portions of the tube as a mixture of sulphate and sulphite. The salt can thus be progressively converted into sulphate.

It has also been found that on keeping for about six weeks the salt is converted naturally into sulphate.

The amount of sulphur in any coal is always found more than sufficient to combine with all the ammonia, and the excess can be absorbed in a lime tower, or, as suggested by Mr. Curphey, Chief Inspector under the Alkali Act, treated with milk of lime, giving calcium bisulphide, for which there is a ready sale.

Difficulties.—The main difficulties of the process were with the revivification of the fouled oxide. The reaction was so violent that the material became red hot and broke down to dust to such an extent as to be useless for further purification. Also the material became acidified with the increasing sulphurous acid content, and had to be washed and dried before further use—a cumbersome operation. These difficulties have been overcome in the later modifications of the process.

LARGE AND SMALL SCALE EXPERIMENTAL PLANTS.

Experimental plants of varying sizes were put up before the war, and many practical details studied and difficulties remedied.

PLANT AT TEGEL.

A plant designed to deal with 300,000 c.ft. per diem was erected at the experimental works of the Berlin Municipal gas undertaking at Tegel, and Dr. Harold Colman inspected it and reported upon it.

Removal of Sulphuretted Hydrogen and Cyanogen.—Five purifiers were installed measuring 6 ft. 6 in. by 6 ft. 6 in. by 2 ft. 6 in., and occupying about 81 sq. ft. of ground space. Three of these were working in series at a time, one being revivified, and the fifth was clean and

ready for use at any moment. The purifiers were divided into five sections or partitions parallel to the longer sides, the partitions of wrought iron being hollow and having water circulating continuously in them, this water conveying the waste heat from the purifiers undergoing revivification to the working purifiers and keeping them at a temperature of about 60° C. The oxide used was in small nodules the size of peas, and gave on analysis :—

Ferric oxide	73·1 per cent.
Combined water	13·9 ,, ,,

During Dr. Colman's visit only 130,000 c.ft. per diem could be supplied to the plant, but during the whole of his eight-day visit this amount of gas was being completely purified from sulphuretted hydrogen by one purifier, which had been working for some weeks (as third and then as second box), and had been fouled and revivified twice before. Official figures showed that three purifiers completely purified 330,000 c.ft. per diem. For this quantity of gas two purifiers were sufficient, and an overload of 10 per cent. could be dealt with for short periods. The back pressure of the gas observed by Dr. Colman was under an inch at each purifier, but would probably be about 2·5 in. when the maximum amount of gas was passing.

Revivification.—It was found that when revivifying by blowing in air some of the sulphur remained as a basic ferric sulphate which, when the gas was again passed through it, formed solid ammonium sulphate and tended to block up the pores of the material, making it less active. To render it suitable the revivified mass was washed with water and dried. To obviate this inconvenient proceeding a mixture of nearly equal volumes of air and water vapour at 80° C. was used instead of air alone, and this kept the temperature during the oxidation of the sulphur lower, and it was found that the mass was then ready for use without washing, only 0·5 per cent. of basic sulphate being found after three foulings. The temperature of revivification was kept below 350° C. by regulating the air supplied, and by the circulation of cooling water in order to prevent the formation of anhydrous ferric oxide, which is nearly inactive to sulphuretted hydrogen.

A change of purifier was necessary when working at full capacity every seven or eight days, and the revivification took about a week.

The absorptive capacity of a thrice revivified material for sulphuretted hydrogen was compared with that of a new unused sample, and it was found to have decreased by 18 per cent. Whether this decrease would go on at the same rate was not known, as the plant had only been working for a short time. The oxide in the five purifiers was expected to last for six months at least. The total expenditure for new oxide at 30s. per ton working out at well under a tenth of a penny per 1000 c.ft.

Ammonia Recovery.—An almost complete removal of ammonia was effected, 320 gr. per 100 c.ft. being reduced to 0·4 gr. (With the ordinary plant in use it is considered good working to reduce the ammonia to less than 1 gr.)

The salt obtained was white and clean, and contained 24·8 per cent. of ammonia and no free acid. To keep up a regular separation of salt the gases from the purifiers being revivified and containing large quantities of steam, had to be well cooled and the water removed before reaching the scrubber, to prevent dilution of the liquor. A gas containing a high percentage of sulphuretted hydrogen, and consequently causing a large amount of water to be formed in the purifier, will also tend to dilute the liquor in the saturator, which may have to be heated slightly so that it will not take up moisture from the gas.

The gas left the saturator at a temperature of 70° C.

Dr. Colman was of the opinion that the process was substantially a practical one, though requiring modifications in revivifying methods. The foregoing figures were obtained by Dr. Colman at Tegel.

These results are as nearly alike as can be expected within the limits of experimental error.

—	Burkheiser Plant at Work.	Ordinary Scrubber and Purifiers.
Coal carbonized	4·72 tons	4·71 tons
Gas made, corrected	56,550 c.ft.	56,410 c.ft.
Make per ton	11,970 ,,	11,970 ,,
Illuminating power, Elster Argand	10·3 candles	10·0 candles
Calorific power, gross	543 B.Th.U.	524 B.Th.U.
,, ,, net	486 ,,	470 ,,
Complete analysis—		
Carbonic acid	2·6 per cent.	2·6 per cent.
Unsaturated hydrocarbons	2·3	2·3
Oxygen	0·2	0·2
Carbonic oxide	11·4	10·9
Methane	26·6	26·1
Hydrogen	54·9	54·0
Nitrogen (difference)	2·0	3·9

PLANT AT POOLE.

An experimental plant capable of dealing with 2 million c.ft. per diem was erected at the Bournemouth Gas and Water Company's works at Poole, but details and particulars of the actual working results were taken by the British Burkheiser Company, which ceased to exist during the war, and the records cannot now be obtained. The plant yielded promising results with the exception of two difficulties.

The first was the fact that the revivification of the oxide and the burning of the sulphur were slow compared with the fouling of the oxide, and it seemed impossible to get the time factors to agree within practical limits. Also it was difficult to get an evenly controlled burning of the sulphur, even with water tubes throughout the mass to control the rate of combustion.

The second and fundamental difficulty was the character of the oxide. The material provided at Tegel was in small nodules which stood the revivification without breaking down into dust, but the supply of this was very limited, and sufficient could not be obtained to supply the Poole plant. The materials obtained all broke down into dust after the first burning, causing so much back pressure as to throw the plant out of action.

Herr Burkheiser had contracted to provide suitable oxide at 30s. per ton delivered, but when it came to the point the oxide was not what was expected.

The plant at Poole was erected on the understanding that payment would be made only if the guarantees were satisfactorily carried out

PLANT AT LIEGE.

A Burkheiser plant was installed at the Flamelle Grand Coke Oven Works, near Liège, which dealt with 2 million c.ft. per diem. It worked well except for revivification difficulties and the difficulty of obtaining suitable oxide.

PLANTS AT BONN AND SKELMANTHORPE.

At these places plants were erected to make ammonium sulphate instead of Burkheiser salt. A catalyzer was used which worked well with a constant sulphur dioxide content, but was not suited to the revivification conditions which prevailed.

THE LATEST DEVELOPMENTS OF THE PROCESS.

The First Modified Form.—As the purification and revivification methods were the difficulty with the original process, a modification was introduced in which the *revivification* was still " dry," but *purification* was made a " wet " process.

Removal of Sulphuretted Hydrogen and Cyanogen.—These were extracted in a rotary scrubber by a wash, consisting of ferric oxide and free sulphur suspended in ammonia liquor. The absorption of the sulphuretted hydrogen was accomplished in two steps; first, the formation of ammonium sulphide, and, secondly, its action on the ferric oxide to form ferric sulphide :—

$$H_2S + 2NH_3 = (NH_4)_2S$$
$$3(NH_4)_2S + Fe_2O_3 = Fe_2S_3 + 6NH_3 + 3H_4O.$$

The sulphur present formed ammonium polysulphide, which absorbed the cyanogen forming ammonium sulphocyanide.

Revivification.—This was not performed in the purifier itself. The sludge from the purifier contained polysulphide and sulphocyanide in solution and Fe_2S_3 and sulphur in suspension. The sulphur was removed in a small standard washer by treatment with ammonium sulphide, which absorbed it, giving ammonium polysulphide and leaving the ferric sulphide in suspension. This was re-

moved by gravity and revivified by hot air in a drum-shaped drying apparatus, giving ferric oxide and sulphur which were used again with fresh liquor. The solution of polysulphide and sulphocyanide was heated to 95° C., when the polysulphide was dissociated, giving ammonium sulphite and free sulphur. The former was used again to take up more sulphur, and the latter burned in a separate kiln to provide the necessary oxides of sulphur. The sulphocyanides were treated with lime at the same time, calcium sulphocyanides being formed and the ammonia released returned with the ammonium sulphide. It was intended to return the calcium sulphocyanide to the retorts, but it was found in practice that the sulphocyanides were decomposed by the steam present forming ammonia, and increasing the ammonia recovered at the expense of the cyanogen.

Ammonia Recovery.—This was carried out as in the original process.

Difficulties.—This process proved to be a success so far as purification was concerned, and the same purification material was in use for four years in the plant erected for the Harpener Gergau A.G. But there were mechanical difficulties in the plant due to grinding, mixing, drying, and revivification of the oxide. Since the continuity of the process was one of its main principles, this upset the whole plant, and a sufficiently long run was not obtained to make satisfactory proof of bye-product recovery possible, and it was realized that further modifications were necessary.

THE FINAL FORM.

In this final modification both purification and revivification were wet; this eliminated most of the difficulties and reduced the mechanical needs to a minimum. The purification and ammonia recovery remained unchanged, but the revivification of the spent material was carried out as follows :—

The sludge containing ammonium polysulphide and sulphocyanide in solution, and ferric sulphide and sulphur in suspension, was treated with concentrated gas liquor (ammonium sulphide) in a closed stirrer, the sulphur taken up and ammonium polysulphide formed. The mixture was passed into a settling tank and allowed to settle, the solution of polysulphide and sulphocyanide drawn off and heated to 95° C. as before, the ammonium sulphide used again, and the sulphur dried centrifugally to be burnt separately for the provision of the necessary sulphur oxides. The unchanged sulphocyanide was treated as before. The ferric sulphide, while still moist enough to be pumped, was mixed with some revivified material to break up the polysulphide and prevent the formation of sulphur-oxygen compounds, and was revivified by an air stream.

THE POSSIBILITY OF THE TECHNICAL DEVELOPMENTS WITH A VIEW TO APPLICATION IN THE GAS INDUSTRY.

This point has been covered in the previous section. The modified plant was examined in 1917 by the German Ammonia Sales Department, who reported that purification was complete, and that "wet" revivification worked satisfactorily. The process has no deleterious effects on the gas, the illuminating power and calorific value being unaltered as nearly as could be ascertained.

The process has many very definite advantages both of cost, space occupied, and ease of manipulation, and solves many present problems, such as the disposal of waste liquor and other such present difficulties.

PROBABLE COSTS IN COMPARISON WITH THE COSTS OF THE PRESENT-DAY METHOD OF AMMONIA RECOVERY.

The Burkheiser plant is a much smaller plant than that in use at present, taking the place of the purifiers and the ammonia plant. Owing to the rapidity with which the gas can be passed through, the purifiers used are much smaller and fewer in number. Indeed, the actual plant occupies only a fraction of the space at present devoted to plant for the same purposes. Moreover, the large amount of ground space required for spreading out the spent material during regeneration by the atmosphere (usually as much again as that occupied by the purifiers themselves) is entirely dispensed with. The initial cost of the plant and the housing of it is, therefore, much less than at present. Repair costs are no greater in proportion.

Since there is no acid used (the liquor being acidic in properties without being acid), no corrosion of the plant takes place, and the upkeep costs of the Burkheiser plant are likely to be less than with the present type. No lead work is necessary, which is also a saving. The difficulties and expense of extension and removal, particularly where the works are situated in a confined space, are greatly reduced.

The labour required to run the plant is no greater than that now employed, nor is more skill necessary than at present. The routine of the plant is simple and easily intelligible to men accustomed to the present plant. The chemical supervision necessary is about the same.

The cost of the sulphuric acid, which has to be bought in large quantities at present for the fixation of the ammonia, is entirely saved, so that the price obtained for the ammonium salt allows of larger profits. The yield of this salt is also increased owing to the conversion of the cyanogen into ammonia, and the fact that no ammonia is lost by evaporation from the liquor tanks.

The quantity of liquor in use in the Burkheiser process being so much less, the room and cost of storage is diminished. Also in works where the liquor is not worked up on the premises, the cost of cartage to the distillers and the distillers' profits are saved.

Finally, the difficulties associated with the disposal of sulphate plant effluents practically disappear.

CONCLUSION AND GENERAL REVIEW.

The Burkheiser process appears to contain the elements of a practical and smoothly working continuous method of gas purification and ammonia recovery. It is likely to eliminate or greatly reduce many present difficulties, such as the disposal of waste liquor, trouble with the small from waste gases and revivifying oxide.

The great and fundamental difficulty so far as the dry process is concerned is the production of a purifying material with suitable physical properties. All materials so far obtained, except that originally used at Tegel, are incapable of standing the rigorous treatment to which they are subjected during revivification, without breaking down into dust at the first burning and becoming useless. The original oxide was obtained from Silesian oxide fields in small quantities by picking out special material occurring with the inferior oxide, and the supply of this very soon gave out entirely.

So far as the wet process is concerned, a considerable amount of research on a small-scale working plant is still necessary, but a study of the work already done suggests that the advantages of a successful process are sufficient to warrant some expenditure of time and money in such work.

Unfortunately the death of Herr Burkheiser appears to have retarded, if not actually stopped, the development of a very promising process.

Mr. C. F. BOTLEY (Chairman of the Committee), introducing the report, said: I have a plan of campaign which perhaps may be acceptable to members. We who are serving on the Ammonia Sub-Committee set out in the first instance to survey the possibilities in regard to this matter. Please understand that we do not for one moment suppose that we have covered everything, but some of the problems which occurred to us we have endeavoured to deal with; and with the help of valuable friends of yours and mine we have reached a certain stage. We want to avail ourselves of this opportunity of pooling knowledge, and I cannot appeal too strongly to everybody to bring their knowledge into the pool. You have already had papers by Mr. Hollings and Dr. Pexton, and I have no doubt that some of the members have availed themselves of the useful information contained therein. With regard to the contribution by Dr. Parker, I should like to say that he began his task before his translation to another sphere. He has completed a paper, though he is no longer a Research Chemist attached to the Committee. This fact is an indication of the interest which he maintains in this work.

Discussion.

Mr. W. B. MCLUSKY (Halifax): May I say that thirty years have elapsed since Mr. Holgate arrived at the same conclusion as that drawn by Dr. Smith in his paper.

Mr. JOHN WILKINSON (Nottingham): When I followed Mr.

on all Carbonising Problems

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Holgate at Halifax I endeavoured to continue the work on which he had been engaged. One-half of the plant had at that time been completed, and I worked that finished half for two or three years. I watched it very carefully, and I can confirm Dr. Smith's experience. We got a good recovery in the liquid purification plant, but I decided not to finish the remaining half of the plant, and went back to ordinary solid oxide box purification.

Prof. Cobb's Process.

Mr. G. R. Thompson (a Representative of Leeds University on the Joint Research Committee of the Institution and the University): I think Prof. Cobb has been unduly pessimistic in his presentation of the account of this process to the Institution. It is a process which, I think, deserves further consideration. About eight years ago the position was that the price of sulphuric acid was falling, the cost of power was high (it has come down very much relatively to other things since then), the price of sulphate of ammonia was abnormally low, relative to pre-war price, and the prospects with regard to ammonia were beginning to look unfavourable because of the offers of synthetic ammonia. Coal costs were high at that time. If you had a producer plant running (say) on the Mond system, you would get a cycle of operations in which the efficiency was possibly 5 p.ct. less than the maximum which you could get out of the producer system. That involves 5 p.ct. extra consumption of coal purely in the producer cycle, in addition to the waste steam which has to be produced to preserve the ammonium sulphate. If you depart from the Mond cycle, you get a richer gas, which offers economy in use. So that anyone who had been using a rather expensive coal and a Mond plant had before him the possibility of saving 5 p.ct. in fuel, and possibly more; as a matter of fact, the ultimate saving of fuel was more than twice that. If you consider all these factors together, you will see that a process which depended for its success upon the saving in the price of ammonium sulphate had no chance. But that is not the position from the Institution of Gas Engineers' point of view. In the case of industrial gas there was no incentive to purification, and no allowance could be made for it. If you consider the process at the gas-works, you will probably have (say) less than half the quantity of ammonia required to precipitate the sulphur with zinc sulphate, or possibly one-third. You will have that quantity to remove, and there is so much less to remove in the sulphide purifier.

In the paper there is an indication that the loss of sulphur in roasting can be made up by the absorption of sulphur with zinc oxide. Well, you have surplus sulphur, and you can get as much sulphur as you want from the process, and a certain amount more. It depends upon how much is lost in leakage from the furnaces, by absorption, and so forth; you have an abundance of sulphur in the gas, and probably an excess, if you work economically. You may say that zinc oxide is a very bad absorber, and that you could not hope to purify the gas with it; but I think that zinc oxide, if activated by a solution of a zinc salt, is a very good absorbent for sulphuretted hydrogen. You can add a little zinc sulphate, and you get then an ammonia-free gas, and absorption of sulphuretted hydrogen by means of zinc sulphate. This gives a slight acidity in the solution. Zinc sulphide will precipitate under those conditions in a granular form, which is easy of filtration.

These dilute solutions are often better absorbents than such things as strong caustic soda. If you try to absorb carbon dioxide, for example, by strong caustic soda, you get a low rate of reaction. With a dilute solution you can get a better rate, but with a very dilute solution you obtain a lower rate of absorption. There is an optimum strength. With a lime solution in water, you get a better rate with several of the caustic soda absorbents, in a bubbling experiment. If you mix lime with dilute caustic soda you can bring about the activation of the lime, and so use the combined absorptive powers of the dilute caustic soda and the milk of lime solution. The absorption of sulphuretted hydrogen with zinc sulphate in the presence of zinc oxide is very satisfactory on bubbling tests. It is not worked out for the complete removal of sulphur, but in the laboratory it promises very great success in the practically complete removal of sulphuretted hydrogen; and this can be done in a plant which occupies very much less space than the box purifiers.

Though Prof. Cobb indicates that oxidation is difficult, this oxidation can go on in a plant. If it were possible to establish a process such as this at the gas-works, you would be able to eliminate the box purifiers, and a good deal of the space formerly occupied by them could be made available for other purposes. The process, as we found it, was not perfect. Ultimately, however, the difficulty boiled down to this—that the oxidation can take place only at a certain rate in a certain volume of liquid when you have perfect aeration. If you have aeration which is not perfect, you get possibly half the rate you should attain. The process slows down as the concentration of zinc sulphate in the solution increases. If the cost of purification could have been given to the plant, I am certain that the history of the work would have been totally different; and I think the Institution should look upon it in that light.

Prof. Cobb: I am glad that Mr. Thompson has made this supplementary statement, because for about two years he was very closely connected with the working-out of the details, and has had good opportunities of studying it and arriving at the conclusions which he has felt justified in stating.

The Burkheiser Process.

Mr. P. Parrish: For seventeen or eighteen years I have taken a deep interest in the Burkheiser process, but in my view it is surrounded by any number of difficulties, and it seems to me that it will need to be simplified very materially indeed if it is to be made suitable for application to the ordinary gas-works. I am not content to accept the statement made by Mr. Moon—I am not attempting to deny his veracity, but I base my opinion on scientific grounds—that the Burkheiser process was unsuccessful merely because it was impossible to reproduce the physical characteristics of the Silesian nodules of iron oxide. Surrounding the problem of the absorption of hydrogen sulphide by iron oxide, and the formation of the sulphide of iron, and the subsequent release or decomposition of that sulphide of iron by air, are all kinds of intricate possibilities. The attempt of Burkheiser was to decompose sulphide of iron under temperature conditions to produce sulphur dioxide, but, depending on the temperature conditions, and depending on the time contact of the oxidation, there is the possibility of sulphite of iron also being formed, and the introduction of more of these precious nodules of Silesian iron oxide in order to continue the process. Further, it seems to me that what ought to have been developed was the possible production of sulphur trioxide. It is conceivable that the hydrogen sulphide of the crude gas would have been absorbed by a special form of iron oxide, sulphide of iron being formed; and then, when the oxidation process was resorted to, it would have been possible to have had such a quantity of iron oxide present that it would have acted catalytically and would have converted the sulphur dioxide which was released into sulphur trioxide. The mechanism of that reaction is very intricate indeed, and I am certain that any amount of work has to be done before one can see any successful issue in that particular phase of the process alone.

This, however, is not the only difficulty in connection with the operation of the Burkheiser process as originally conceived. Assuming there was no difficulty in the formation of sulphur dioxide, and that sulphur dioxide was absorbed in the sulphurous acid formed, and assuming also that a certain amount of trioxide was formed, giving a mixture of sulphite and sulphate, and that the ammonia was absorbed cyclicly as ammonium sulphite and ammonium sulphate, and as ammonium bisulphite and bisulphate, one is then face to face with the precipitation or crystallization of the Burkheiser salt such as Mr. Moon represents it in this paper. I have spent at least three years on the oxidation of Burkheiser salt. I have been able to produce it without any difficulty whatever from the combustion of spent oxide and the combination of ammonia distilled in a certain way. But it is a very difficult matter to oxidize a mixture of ammonium sulphate and sulphite in order to obtain a product which is wholly ammonium sulphate. It is quite true that the oxidation goes very rapidly indeed up to the equilibrium point; but immediately the equilibrium point has been reached, the oxidation, even with ozonized air, carried out under conditions which are calculated to bring about the best possible oxidation, does not admit of the conversion of the whole of that Burkheiser salt into ammonium sulphate. I join issue with Mr. Moon when he suggests that there is no deleterious effect due to the presence of ammonium sulphite in the ammonium sulphate. All the experiments I have carried out—and I have made any number of pot experiments to determine whether ammonium sulphite is injurious as a fertilizer—have led to results contrary to those of Dr. Weiler, and have proved definitely that the presence of even minute traces of ammonium sulphite is distinctly disadvantageous to the success of the plant. It is on these grounds that I do not anticipate that we can place very much hope in the development of the Burkheiser process so far as the gas industry is concerned.

More About Burkheiser Salt.

Dr. A. Parker: I would not go quite so far as Mr. Parrish, and say that there is practically no hope; but I agree that an enormous amount of physico-chemical work will have to be carried out before a process so complicated—and it is very much more complicated than it appears to be at first sight—can be made a success. The problem of making ammonium sulphate, and not merely a Burkheiser salt (which contains also sulphite and possibly some thiosulphate), is a very difficult one, and involves an enormous amount of work in phase-rule physical chemistry, and, therefore, is a complicated chemical process. One has to remember that gas-works are not really suited to highly complicated chemical operations. I should, however, like to draw attention to the fact that the process is being studied on fundamental grounds at the present time in Germany; and a paper on the subject, one of the authors of which is, I believe, Dr. E. Terres, has been published in instalments in recent numbers of "Das Gas- und Wasserfach." I have seen the first two parts, though not the third (which I believe is the last, and was published in Germany a week or two ago). The paper involves a consideration of equilibrium and various factors affecting the percentage of ammonium sulphate.

Mr. Moon: I feel that, if my paper has done nothing more than to bring out the observations we have just heard from Mr.

Parrish and Dr. Parker, it has justified its existence. They are contributing further knowledge, which is exactly what we want.

Mr. BOTLEY: I think the Burkheiser process is one from which some good might evolve. I have a statement in connection with the Koppers C.A. process, and in the introduction the writer states:

> A great number of chemists have tried different experiments to work out gas cleaning by the wet process. They are all related, in the form of iron or other metals, but without any results. At the beginning of this century two new methods were tried to solve this problem. The first was that of Burkheiser. He worked to remove the hydrogen sulphide from the gas through a kind of iron-containing dry cleaning mass, and to renew the mass by roasting it again. Hereby the sulphur is transformed into sulphurous acid (SO_2) partly, and anhydric sulphuric acid (SO_3). Both these recovered products are used to make ammonium salts with the ammonia contained in the gas. The produced salt consists in the main of ammonium sulphite $(NH_4)_2SO_3$, and contains besides quite a large amount of ammonium sulphate.

This is striking confirmation of what Mr. Parrish has said.

ADMISSION OF STEAM TO VERTICAL RETORTS.

Dr. A. C. MONKHOUSE: I can confirm what Mr. Hollings has said about the admission of steam to vertical retorts reducing the maximum strength of liquor obtainable. I have figures showing that in vertical retorts, producing a 475 B.Th.U. gas, using, for washing, only about 1 gallon of water per ton of coal carbonized, the maximum strength obtained is 9 oz. It does show that, as the calorific value of the gas produced is diminished, there is a very much greater volume of liquor to deal with, due to the undecomposed steam which passes through the retorts.

NEED FOR GENERAL ENTHUSIASM.

Mr. W. W. TOWNSEND (Colchester): As a member of the Committee, I feel that we shall have wasted an opportunity if this discussion does not lead to something rather more definite than we have heard so far. I think the Committee require from the Institution a mandate to go on and really to accomplish something in regard to the ammonia question. We have been dealing with the matter for about eighteen months, and I think the time has been very well spent, as you will have noticed from the papers and discussion. At the moment I think the Committee has justified its appointment. It has had very little backing so far, however, from the members of the Institution. There is far too much of a tendency—which seems rather likely to be encouraged by what has been said to-day—to think that our present methods of washing gas for the removal of ammonia, and our present methods of producing sulphate, are the best that can be evolved, and that all other processes involve a vast number of technical difficulties which are likely to be insurmountable. Therefore, the conclusion of the argument is that, barring incidental economies such as Mr. Hollings has suggested in his very able paper (and which are not by any means to be despised), we have to look forward to a continuance of our present methods. When this Committee was set up eighteen months ago, there were a few people who thought it was worth while taking a little trouble and spending a little money in order to find out whether or not that was in fact the case. I am a member of the Committee, and it is not my place to do this, but I suggest that some member of the Institution should urge the Committee not to be afraid to spend a little money, even in investigating the Burkheiser process, which has an obvious fascination. The Institution has funds at its disposal, and I suggest that this is a subject on the investigation of which an expenditure of a few hundred pounds may very likely produce a return of many thousands.

NEW BYE-PRODUCT SULPHATE PROCESS.

With the President's permission, I should like to refer to something which may not have come to the notice of the members, and that is a report, in the "Chemical Age" dated Nov. 2, of a new bye-product sulphate process invented by a German chemist, Dr. Tern, the use of which process obviates the necessity to buy sulphuric acid outside, and enables one to utilize the sulphur in the spent oxide. The washing of the gas is done in the ordinary way, the ammonia is driven off in stills by steam, and then the necessary sulphur is obtained by burning spent oxide, which forms sulphur dioxide, which is then converted. It is said that the process is simple and very economical, and that installations having the capacity for an output of 37,000 tons per annum are projected in Germany. Also, a large plant has been in operation since the beginning of July at the gasworks at Engelsdorf bei Leipzig. The cost of production of the sulphate, which is called "Elektroammon," is said to be from 90 to 100 reichmarks per 1000 kg. less than that of ammonium sulphate as hitherto prepared. Translating this into English currency, I come to the astounding figure of something like £4 10s. per ton. I do not vouch for this, but it shows that other people are trying to solve the problem; and it is up to this Institution to try to evolve some process itself. There is one great drawback of the process I have just mentioned, and that is that there is still the trouble in respect of effluent liquor. We want a process which will remove that difficulty while at the same time reducing the cost of extraction of ammonia.

The PRESIDENT: I do not know whether Mr. Townsend was blaming the members of the Institution generally, or the Council, for this slackness in regard to ammonia research, but he is a member of the Council and also a member of the Finance Committee, and at our last meeting we were able to speed up this work. We have some money, and we are helping these various Committees to get more done by increasing the staff. I should not like the suggestion to go out from this meeting that the Council of the Institution are holding back research.

Mr. TOWNSEND: I had no idea of criticizing either the Ammonia Sub-Committee or the Council. I was asking the general members of the Institution to give us a mandate, because I think the members of Council need encouraging when they are thinking of spending hundreds of pounds.

Mr. WILKINSON: The matter now under consideration cannot be dealt with in a few months at the cost of a few hundred pounds. Probably the Chairman of this Committee will remember that at their first meeting I said that this work would occupy years, and would cost thousands of pounds. None of the matters which has been introduced at this meeting or at any of our Committee meetings is new. I daresay the majority of the members of the Institution have burned their fingers more or less severely from time to time in trying to deal with these problems, but we have not been able to get at the bottom of things as ordinary engineers. We have now come to realize that, if we are to fathom these difficulties, we have to get the scientific experts working; and we must not expect them to solve the difficulties in a few months, on an expenditure of a few hundred pounds. If we do not solve the difficulties until ten years hence, all the money and trouble devoted to the problems will have been well spent.

WHAT IS THE MAIN OBJECT OF THE RESEARCH?

Mr. T. GLOVER (late of Norwich): It is not clear to ordinary members of the Institution what is the main object of this research. I was under the impression that it was to find more profitable outlets for our nitrogen products, but we seem to have been concerned more with the investigation of systems of purification by means of ammonia. I would point out that any system of purification by means of ammonia, adopted to provide a use for our ammonia—*i.e.*, to absorb ammonia so that we do not have to set it free—would not be regarded as a perfect process. If we use ammonia for purification, we use it as a medium of purification and not for its ultimate absorption, so that the development of all these processes—the Burkheiser, the zinc process, or the liquid ammonia purification—does not mean that we have found profitable outlets for the nitrogen which we are bound to produce. Therefore, I hope the Committee will not lose sight of the main object, which is to remove the difficulties which many works are experiencing in disposing of their nitrogen products in the way of ammoniacal liquor or salts made from ammoniacal liquor.

It appears that perhaps we have also lost sight of the fact that these weak liquors which are associated with the carbonization of coal in vertical retorts can be concentrated and made much more marketable by the use of steam obtained by means of waste heat. In all modern installations of vertical retorts waste-heat boilers have been installed, and there is any amount of steam available for use in the concentration of the liquor. It can be concentrated up to 15 p.ct. of ammonia, or even higher, thereby reducing the weight of the liquor, and so reducing the cost of carriage and the ultimate cost to the consumer. This question of the profitable or unprofitable disposal of our nitrogen in the useful form of sulphate of ammonia is wrapped up with the cost of sulphuric acid, and the cost of sulphuric acid varies considerably in different parts of the country. It is not so much a matter of scientific research as of commercial research; and I suggest that it is worth the while of the Committee to investigate the reasons why the cost of sulphuric acid varies so much, and why it is so high in many parts of the country as to render the manufacture of sulphate of ammonia an unprofitable process.

REMOVAL OF TAR FOG.

I agree with the remarks of Mr. Hollings with regard to the making of strong liquor and the better liquid purification of the gas, not by caustic ammonia, but by the addition of the least quantity of water, so as to obtain the greatest strength of the liquor at the outlet from the washer. Recently, I had a good deal of experience in the use of a static washer where the tar from vertical retort gas is abundant as tar fog; and this was removed in the lower part of the washer. There was effective removal of ammonia in the upper part of the washer, partly because of the very efficient removal of tar fog in the lower part. In the lower part of a three-tier washer—or of any other washer, though I would not recommend less than three tiers—the tar fog is so effectively removed that the clean water in the upper tiers is able so effectively to remove the ammonia that a 12-oz. liquor is produced from the lower tiers, and also, of course, there is a constant stream of tar. I think this is a matter we have not emphasized sufficiently—the splitting-up of the gas into very fine streams does help considerably to remove the tar fog which enshrouds the molecules of gas and prevents

the water removing the ammonia effectively. There are some forms of washer in use which are extremely inefficient from the point of view of the removal of tar fog; and if we do not remove it, we do not give a fair chance to that part of the plant which is devoted to the removal of ammonia. It is necessary that we should consider these matters, and I do not think we have wasted time by reviewing the position with regard to processes of manufacture. It is only the foundation, I believe, of further work with a view to finding better outlets for our nitrogen.

Plant at Stretford.

Lieut.-Col. W. M. Carr (Stretford): Mr. Hollings refers to the final extraction of ammonia by the use of weak liquor—*i.e.*, without the addition of any water in the process. This, I think, is a big advantage, and it is a method which I am endeavouring to develop, using weak liquor containing fixed ammonia only, but cooled before use. My plant is not yet installed, so that I cannot give figures, but I hope that in twelve months' time I shall be able to give results. I should like to ask if Mr. Hollings is using for final washing a weak liquor containing free ammonia, or if it contains only fixed ammonia.

A Paper of Great Value.

Mr. D. M. Henshaw (Messrs. W. C. Holmes & Co., Ltd.): For a few years we have tried to work, as part of our contractors' business, some little research organization; and we have tackled some of the problems discussed in this paper. I should first like to congratulate Mr. Hollings and Dr. Pexton on a paper which, I venture to suggest, is of greater value immediately to your industry than anything which has been published before in its history. I do not think there is any text-book, or any article or paper, in which the actual physical principles which are really at the bottom of the successful working of plant of this description have been explained in such a practical way. There, I think, we have an explanation as to why this kind of work has not been done so successfully before. It is that Mr. Hollings and Dr. Pexton have had the advantage of working on plants which can be run to their maximum capacities, where steam pressures, water temperatures, and all the other complex conditions which enter into the securing of an efficient result can be carefully controlled. The owners of works of this size, of course, are in a position to give that service to the industry. It is often difficult to try out a plant to its full capacity, because, when a plant is installed, there is a considerable margin allowed between actual output and capacity, very much greater than the margin which Mr. Hollings suggested; and in many cases the plant probably becomes worn out, or becomes inefficient through the natural decay of some part or other, before the ultimate capacity has been reached.

These papers, surveying as they do the present conditions of the working of plants, form a very good foundation for the work which I hope your Committee will carry out in the future; and when you take into consideration the vast amount of capital which is sunk in the gas industry, you are certainly entitled to spend some money and time on these problems. The use of cool fixed-ammonia liquor for washing will enable gas-makers to overcome the difficulties arising from the use of hard water; and there are a number of other advantages arising from the use of this liquor. If this were the only thing arising from your investigations as a Committee, I think these investigations would have been worth while.

With regard to the process which is being developed in Germany, I think that, particularly in these days of improved international relationships, we should do all we can to keep in touch with developments. There may be some who do not like the idea of making use of foreign developments, but, on the other hand, we should not like people in other countries to consider that anything we might be doing is not worth while merely because it is English. The German people have spent a lot of money and have trained men for this particular work; and we should endeavour to do likewise.

Direct and Semi-Direct Ammonia Recovery.

Mr. A. L. Jennings (Cleckheaton): I think that one of the greatest services the Research Committee can render the gas industry is to follow up the investigations into the processes of recovery of ammonia, for the commercial advantage of the industry. Ammonia used to bring in the equivalent of about 2d. per 1000 c.ft., but nowadays it brings in practically nothing. The price of 10-oz. liquor has been as high as 15s. 6d. per ton, but nowadays it is about 1s. 6d. or 1s. 0d.; and if there are carriage charges to be paid, there is no advantage in selling it. I should imagine that there are no great possibilities commercially in the manufacture of sulphate or the concentration of ammonia in gas-works to-day unless plant is already installed. The steaming of vertical retorts (which used to produce 11-oz. liquor), though the steam may be superheated to 600° C., results in a big volume of weak liquor. I can see no possibility of turning that liquor (say, 7-oz. strength) into a commercial proposition by recovering ammonia with the sulphate plant; neither can I see that the expenditure incurred in installing concentrated ammonia plant would be justified. It seems to me, therefore, that the course which is most likely to prove productive is for the Research Committee to devote attention to the possibilities of making a commercial success of the direct or semi-direct method of making sulphate.

A Speaker: It seems to me that, generally speaking, the difficulty about making sulphate of ammonia commercially in gas-works is that the individual works are too small, because you must remember that you are up against people who are going to make ammonia in thousands of tons per week. Indeed, at the works of Imperial Chemical Industries, Ltd., there has just been installed a large coke oven plant; and I have been told by somebody who has been to those works that the ammonia in that plant was considered as being of absolutely no account, owing to the vast quantity of ammonia that is being produced synthetically. It seems to me that one of the things the gas industry will have to consider will be the combination of the small works, a course which is now being adopted on the Continent with success. I believe the bye-product coking industry in this country has already found that works with 15, 20, or even 50 ovens are too small, and they are coming to large works which will ultimately carbonize several thousand tons of coal per day. It seems to me that the gas industry will have to consider such combination as a solution not only of the ammonia problem, but of several of its problems.

Mr. Botley: I should like to make it clear that the members of the Committee have no such limited perception of their duties as seems to be indicated by some of the speakers. If you will read the introduction to the first Report you will see that we are to investigate the commercial possibilities. In dealing with the latter, surely it is pertinent to inquire how we can reduce the costs of operation at the works, as Mr. Hollings has done; surely it is pertinent to inquire whether there are other methods of producing sulphate. We are doing all these things. I have a paper by Mr. P. Parrish, a member of the Committee, concerning the use of calcium sulphide in place of sulphuric acid, which might have been dealt with had time permitted.

Mr. Hollings' Reply.

Mr. Hollings: On behalf of Dr. Pexton and myself, may I express my appreciation of the way in which this paper has been received. Particularly I should like to express appreciation of Mr. Henshaw's remarks. I will deal specifically with the remarks made concerning this paper, and not with the work of the Committee as a whole. I have no experience of the standpipe system to which Mr. Carr refers. I gather that he proposes to take the liquor coming away from that standpipe and to cool it, and then to use it in place of water in the washers. It may be that with his system he will have a sufficient bulk of liquor, but our experience has been that, with the ordinary ascension pipe and hydraulic main, the bulk of the liquor is too small, and we have found it necessary to increase the bulk of weak liquor available by carrying out some process of fractional condensation and by cooling the primary condensate and using it as a substitute for water. The normal quantity of free ammonia in the primary condensate is equivalent to about 1·5-oz. strength. As I mentioned in a paper which I presented to the Institution a year ago, in using it in the washers it is necessary to ensure that the temperatures of the liquor and of the gas are as low as possible—preferably 60° Fahr. One uncertainty with regard to the process is the capacity of washer that will be necessary when pure water is substituted by weak liquor; and this I regard as a matter for further investigation. I agree with Mr. Glover's remarks concerning the necessity for the complete removal of tar fog before the gas enters the washers.

The President: I think this is one of the most interesting sessions we have had. Yesterday's meeting was a great success, and this morning we have not nearly talked ourselves out. Valuable information has been obtained as the result of these discussions on research; and I think it possible that in the future we may meet not merely twice a year, but three, four, or even five times a year.

Before we adjourn, I should like to read to you two letters we have received. One is from Mr. Leather, in response to the telegram we sent him yesterday expressing our sympathy in respect of the accident which he has suffered. The letter is dated Nov. 13, addressed to Mr. Price, our Hon. Secretary:

> Please thank the President and Council for their kind expression of sympathy. I am deeply touched by this and the many other messages I have received. What a number of friends one has! The doctors are quite satisfied with my progress so far.

The second letter, addressed to myself, is from Mr. Henry Woodall, and reads as follows:

> It is with much regret I am unable to attend the Charter Dinner on Wednesday next. You are celebrating an important event in the history of gas engineering, and I should like to take part in it. My uncle, Mr. Henry Woodall, now in his 91st year, is, I believe, the oldest gas engineer living, and, I think, the only surviving member of the original British Association of Gas Engineers, whose first meeting was held in 1863.
>
> I regret to say he is too unwell to go out just now, but I am sure he would have much liked to attend the dinner and given you his support. He is proud to think of the growth of the Institution he helped to start in 1863, and that that small body is now a large and important one, with the distinction of a Royal Charter.
>
> Again expressing my regret at my inability to attend what, I am sure, will be a most enjoyable and successful function.

FOURTH REPORT OF THE LIQUOR EFFLUENTS RESEARCH COMMITTEE.

Presentation and discussion of the Third and Fourth Reports of the Liquor Effluents Research Sub-Committee formed the closing session of the meeting on the afternoon of Nov. 14. The Third Report was published in the "JOURNAL" for June 12, and a section of the Fourth Report is a reprint of the report on the activities of the Emscher Commission given in the "JOURNAL" for Aug. 21 last.

MEMORANDUM ON PROCESSES FOR THE REMOVAL OF PHENOL FROM AMMONIACAL LIQUOR AND EFFLUENT SPENT LIQUORS.

By A. PARKER, D.Sc.

INTRODUCTION.

The principal objectionable constituents of ammoniacal liquor are phenols, higher tar acids, thiocyanate and thiosulphate. When ammonia liquor is distilled these constituents are afterwards found in the effluent spent liquors, though in a less concentrated form if the spent liquor from the still and the devil liquor are admixed, since dilution occurs by the condensation of the steam used for the distillation.

The oxygen absorption capacities of gas liquor effluents, as determined by N/80 potassium permanganate solution at 27° C., are usually employed to indicate the relative polluting effects of these effluents if discharged into streams or sewers. According to this test, the phenols and higher tar acids present in ammoniacal liquors and gas liquor effluents generally account for more than 50 per cent. of the total oxygen absorbed values. This fact is illustrated by the figures that are taken from the Sixty-First Annual Report of the Chief Inspector of Alkali Works and from the Second Report of the Liquor Effluents Research Committee of the Institution of Gas Engineers.

Ammonia Liquor from Storage Well.

—	1. Horizontal Retorts.		2. Vertical Retorts.		3. Vertical Retorts.	
	Parts per 100 by Weight.	Oxygen Absorbed Parts per 100.000.	Parts per 100 by Weight.	Oxygen Absorbed Parts per 100.000.	Parts per 100 by Weight.	Oxygen Absorbed Parts per 100.000.
Thiocyanate as CNS	0·240	195	0·216	180	0·782	647
Thiosulphate as S	0·072	60	0·045	40	0·192	164
Monohydric phenols as C_6H_5OH	0·162	290	0·327	580	0·293	522
Other bodies including higher tar acids	..	65	..	330	..	309
Total		610		1130		1642
O/A per cent. of total—						
Monohydric phenols		47		51		32
Other bodies including higher tar acids		11		29		19

NOTE.—1 and 2, Sixty-First Alkali Report. 3, Hinckley Gas-Works, Original Conditions, 2nd Report Effluents Research Committee of The Institution of Gas Engineers.

These figures show that of the oxygen absorbed values of the particular samples, 32 to 51 per cent. was due to monohydric phenols and 11 to 29 per cent. to other bodies including higher tar acids.

The experiments at Hinckley have demonstrated methods of reducing the quantities of thiocyanate, thiosulphate, and higher tar acids. With the installation of a tar extractor supplied with sprays of liquor, and as a result of certain modifications in the operation of the condensing and scrubbing plant, the composition of the liquor at Hinckley was improved to the extent indicated by comparison of the following figures, taken from the Second Report of the Committee, with those given in the previous table :—

Ammonia Liquor, Hinckley Gas-Works.

[Tar extractor in operation and other modifications.]

—	Parts per 100 by Weight.	O/A Parts per 100.000.
Thiocyanate as CNS	0·499	413
Thiosulphate as S	0·102	87
Monohydric phenols	0·337	600
Other bodies	..	224
Total	..	1324
O/A per cent. of total—		
Monohydric phenols		45
Other bodies		17

The total reduction in the quantities of thiocyanate, thiosulphate, and other bodies which resulted from the installation of the spray tar extractor and from other modifications was equivalent to 396 parts of oxygen absorbed per 100,000.

The experiments at Hinckley have been continued (*vide* Third Report of Effluents Research Committee), and further improvements in the composition of the liquor as regards thiocyanate, thiosulphate, and higher tar acids have been obtained. The experiments included the investigation of an electrostatic tar precipitator installed in the hot foul gas main of a new setting of continuous vertical retorts. This apparatus was highly efficient as a tar separator, reducing the higher tar acids in the liquor to a comparatively small amount. The liquor was much paler in colour, but its content of monohydric phenols was increased, and there was no reduction in its total oxygen absorbed value. The problem to be solved, therefore, becomes principally that of the removal of phenols. Further, the satisfactory removal or recovery of phenols would be almost the only problem of effluent disposal if present methods of ammonia recovery in gas-works were for any reason replaced by certain other methods which have been suggested. For example, in a sample of liquor taken from the condensers of a coke oven installation operating direct ammonia recovery, the monohydric phenols accounted for more than 90 per cent. of the oxygen absorbed value of the liquor (*vide* First Report, Effluents Research Committee).

It is clear, therefore, that the removal of phenols is a subject of considerable importance in the work of the Effluents Research Committee. The various methods suggested may be classified as follows :—

1. Recovery of phenols from ammoniacal liquor or effluent spent liquor by means of solvents, such as benzole, trichlorethylene, dephenolized light tar oil, &c.

2. Recovery of phenols from ammoniacal liquor or effluent spent liquor by solid absorbents—*e.g.*, activated carbon.

3. Removal of phenols by volatilization.

4. Extraction of phenols from crude coal gas at temperatures above the dew-point of the gas before liquor condenses.

RECOVERY OF PHENOLS FROM LIQUORS BY SOLVENTS.

Many patents have been taken out for processes of this type, and several plants are in operation in America and Germany.

In general, according to such processes, the ammoniacal

liquor or effluent spent liquor* is extracted for phenols by washing with a suitable solvent, usually benzole. The solution of crude phenols thus obtained is separated by gravity from the treated liquor. The phenol is then separated from the solvent either by (*a*) removal of the solvent by distillation, or (*b*) extraction with aqueous caustic soda whereby a solution of sodium phenolate is obtained. The sodium phenolate is acidified with sulphuric acid, carbon dioxide, or other convenient reagent, and the crude phenol liberated is separated by gravity.

The methods of operation might best be illustrated by brief descriptions of typical plants.

America.—The plant in operation at the works of the Domestic Coke Corporation, Fairmont, W. Virginia (H. E. Jones, Chem. and Met. Eng., April, 1928, **35**, 215), includes two phenol extraction towers, constructed of steel, and 6 ft. in diameter.

The first tower is 36 ft. and the second tower is 34 ft. in height. Each tower has a liquor distributor at the top and a similar distributor for solvent at the bottom. The distributors consist of inlet pipes and perforated plates with holes of ⅜ in. diameter. In each tower, three beds (each 3 ft. in depth) of 2 in. graded coke are supported on wire screens to serve as mixers and distributors. The difference in height of the two towers permits of gravity flow. Crude liquor flows downwards in series through the first and second towers, to a dephenolated liquor storage tank. Benzole enters the bottom of the second tower and leaves the top of the first tower, so that counter-current flow is obtained. The extraction efficiency for phenol is stated to be 96 per cent. with a liquor flow of 1800 gallons per hour.

The solution of phenol in benzole enters a distributor at the bottom of a caustic soda washer 14 ft. high and 5 ft. in diameter, and then travels through a second similar washer. The washers are charged at the outset, a little more than half full, with a 23 per cent. aqueous solution of caustic soda. The volume of soda increases as phenol is absorbed. The benzole liberated in this manner is recirculated through the phenol extraction towers. It is advisable to redistil the benzole every six months to remove accumulated tarry matter. A certain amount of emulsion forms at the bottom of the soda washers; this is withdrawn periodically and pumped to the neutralizing tank. The benzole from the second washer contains 0·01 per cent. phenol.

The sodium phenolate solution contains cresols, higher tar acids, pyridine, naphthalene, and benzole. The solution is distilled with closed steam to remove benzole, which is condensed and run into the benzole circulating tank. Live steam is then used, and certain impurities are driven to atmosphere.

The crude phenol is liberated from the sodium phenolate solution by the addition of sulphuric acid (sp. gr. 1·71), the charge being agitated by a supply of air. The neutralizing tank is 12 ft. high and 6 ft. 6 in. in diameter. When the sodium phenolate has been neutralized, separation is allowed to take place; the phenol then rises to the top and the solution of sodium sulphate is run to waste.

The crude phenol has the following approximate composition :—

Phenol	54 per cent.
Cresols	23 ,,
Water	16 ,,
Tarry matter	7 ,,

The dephenolated liquor carries away a certain amount of dissolved benzole. For example, at 40° C. ammonia liquor dissolves 0·14 per cent. of its volume of benzole, and 0·16 per cent. at 23° C. The amount of benzole lost in this manner, therefore, might be equal to one-half of the amount of phenol recovered, in which case it would constitute an important charge on the process. With the particular installation described, however, the benzole vapour carried forward when the liquor is subsequently distilled for ammonia, is admixed with coke-oven gas before the gas travels through benzole washers.

It has been stated that this phenol recovery process pays for itself.

* Effluent liquors should be rendered neutral or slightly acid before extraction for phenol.

Plants similar to that at Fairmont, W. Virginia, have also been erected at the works of the National Tube Company, Lorain, Ohio; Iroquois Gas Corporation, Buffalo, New York; and Hudson Valley Coke and Product Corporation, Troy, New York.

R. M. Crawford (Ind. and Eng. Chem., 1926, **18**, 313), describing the operation of the installation of the Hudson Valley Coke and Production Corporation, Troy, New York, states that the sodium phenolate solution obtained also contains cresols, higher tar acids, benzole, pyridine bases, and naphthalene. The benzole, pyridine bases, and naphthalene are largely removed from the phenolate solution by steam distillation.

The benzole employed in the benzole extraction towers also extracts pyridine bases. A portion of the benzole, therefore, is removed continuously from the system and is passed through a washer containing dilute sulphuric acid to remove pyridine bases; the pyridine sulphates are replaced periodically by fresh acid.

The phenols are liberated from the steamed phenolate solution by sulphuric acid, carbon dioxide, or sodium bicarbonate.

REQUIREMENTS.—With 1000 gallons of liquor containing 0·2 per cent. phenols by weight.

Caustic soda (100 per cent. NaOH)	14 lbs.
Benzole (loss)	5 ,,
Sulphuric acid (sp. gr., 1·84)	17 ,,
or carbon dioxide	9 ,,

PRODUCTS.

Crude phenols	16·6 lbs.
By use of carbon dioxide—	
Sodium carbonate	18 ,,
By use of sodium bicarbonate—	
Sodium carbonate	36 ,,

ANALYSIS OF CRUDE PHENOL.—Volumes per cent.

Phenol	51 per cent.
Cresols	26 ,,
Higher acids and residue	11 ,,
Water	12 ,,

In a later communication (Ind. and Eng. Chem., 1927, **19**, 128) R. M. Crawford states that the plant at Troy, N.Y., gives an average extraction efficiency of phenol of 95 per cent. The use of carbon dioxide for neutralizing the sodium phenolate solution had been discontinued and replaced by crude sodium bicarbonate, firstly, because neutralization with bicarbonate can be completed more rapidly, and, secondly, because the amount of spent sodium bicarbonate solution more nearly reached the total make-up needed to supply a unit in operation for the liquid purification of coke oven gas.

Crawford also suggests that an improvement might be made by neutralizing the phenolate solution with sulphuretted hydrogen in place of carbon dioxide. The spent liquor would then consist of a solution of Na_2S and NaHS. This spent liquor, when heated or steam distilled, would evolve H_2S and leave a solution of Na_2S which would then be employed to dissolve phenol. The following cycle of operations thus results :—

1. $2C_6H_5OH + 2Na_2S \rightarrow 2C_6H_5ONA + 2NaHS.$
2. $2C_6H_5ONa + 2NaHS + H_2S \rightarrow 2C_6H_5OH + Na_2S + 2NaHS.$
3. $Na_2S + 2NaHS$ (heated) $\rightarrow 2Na_2S + H_2S.$

Reaction 1. Reaction 2.

Mechanical losses would be replaced by the addition of sulphuretted hydrogen and caustic soda. Crawford is of the opinion that a small profit above operating charges would be obtained.

In a further communication (Ind. and Eng. Chem., 1927, **19**, 966) Crawford states that one important item in the cost of the process results from the loss of benzole by vaporization and by solution in the extracted liquor. The whole of the benzole dissolved in the liquor is not lost, since when the liquor is distilled for ammonia, the benzole is vaporized and is passed into the stream of coal gas before the gas enters benzole washers.

The benzole may be replaced as a solvent, however, by light tar oil, obtained by the distillation of coke-oven tar and washed with 10 per cent. aqueous solution of

caustic soda until the tar acid content is less than 1 per cent.

An examination of a sample of light tar oil used in the process gave the following results :—

Specific gravity at 30° C.	0·953	
Light tar content	0·6	per cent.
Distillation—		
Below 170° C.	18	,,
,, 190° C.	41	,,
,, 210° C.	61	,,
,, 235° C.	73	,,
,, 300° C.	83	,,
Residue and loss	17	,,

With a solvent to liquor ratio of 1 : 1 in laboratory experiments, this oil extracted 93 per cent. of the phenols, as against 73 per cent. with benzole. The light tar oil did not produce any emulsion, and caused a substantial reduction in the red colour of the liquor.

Germany.—P. Francke (Chem. Zeitung, 1925, **49**, 325) has described processes for the extraction of phenols from ammoniacal liquor and effluent liquors, as developed by Gewerkschaft Stinnes, Die Maschinenbau A.-G., Elsass, Bochum, Die Posseyer Meguin A.-G., Essen and Butzbach and Bamag Meguin A.-G.

With effluent liquor, lime is allowed to deposit in a settling tank, after which the liquor is made neutral or slightly acid before entering the extractor, which consists of a cylindrical tank provided with a stirrer. In the extractor, the liquor is agitated for several minutes at ordinary temperature with an equal volume of benzole. Separation by gravity is then allowed to take place and the extracted liquor is drawn off. The solution of phenol in benzole is aferwards mixed in the extractor with a solution of caustic soda. After standing for a short time, the solution of sodium phenolate thus obtained is removed for the recovery of phenol by acidification. The benzole remaining in the extractor is used for treatment of the next batch of effluent.

Ammonia liquor may also be extracted for phenol in the same manner as described for effluent liquor, or other types of plant may be employed. One type consists of a benzole still and an extraction tower. The tower is divided into three superimposed sections. The upper portion of each section is filled with wood shavings or other suitable packing. The top section is supplied with a spray of liquor and with benzole vapour from the still. The benzole condenses in admixture with the liquor and runs into the lower portion of the section, where separation of the partially extracted liquor and the solution of phenol in benzole takes place. The partially extracted liquor flows to the second section of the extractor, and undergoes the same treatment as in the first section, and the liquor from the second section enters the third section for final extraction before passing to the dephenolated liquor storage tank. The benzole solution of phenol from each of the three sections enters an auxiliary separator (in which entrained liquor separates) and then flows to the benzole still in which benzole is again vaporized and crude phenol remains.

In a third process described by Francke, ammonia liquor preheated by passage through the condenser of a benzole still is sprayed into the top of an extraction tower filled with Raschig rings; and benzole vaporized from the still and afterwards condensed enters the extraction tower at the bottom. The benzole rises through the liquor in the tower and extracts phenol. The solution of phenol in benzole collects at the top and overflows to the still, and dephenolated liquor flows away from the bottom of the tower. The phenol which collects in the still is withdrawn periodically.

Francke gives the following estimate for treatment of 100 cubic metres (22,000 gallons of liquor containing 0·5 per cent. phenol of which 90 per cent. is extracted).

450 kg. (990 lbs.) phenol	180 M.
6 tons steam for vaporizing 30 c.m. benzole	18 M.
Wages	6 M.
Leaving for sinking fund and depreciation	156 M.

It should be noted that no estimate is given to account for benzole dissolved in and carried away by dephenolated liquor, and for other working losses.

Francke also mentions that trichlorethylene may be employed in place of benzole. Trichlorethylene possesses the advantage of being non-inflammable, and is less soluble than benzole in the treated liquor.

In an article in the "Gas World" (1926, **85**, Coking Section, July 3, pp. 20-22) a description is given of a plant erected at Hattingen by the Bamag-Meguin A.-G. The ammoniacal liquor flows through coke filters to remove tar, is preheated to 65° C. by benzole vapours from a still, flows to a mixing pump to meet benzole partly enriched with phenol and thence to a separating tank. The partially extracted liquor flows to a second pump, where it mixes with clean benzole, and then passes after separation to the ammonia still. The solution of phenol in benzole is heated to 80° C. (B.P. of phenols, 180° C.) in a still from which the benzole vapours pass through a rectifying column and dephlegmator and are cooled by liquor on its way for extraction. The phenol tar remaining is distilled to remove the last traces of benzole. The average phenol content of the liquor employed is 0·3 per cent., and this is reduced to 0·07 per cent., equivalent to an extraction efficiency of 75 to 80 per cent. The crude carbolic tar obtained has the following composition :—

CRUDE CARBOLIC TAR.

Phenols	64·3 per cent.
Bases	8·8 ,,
Neutral oils	21·9 ,,
Water	1·0 ,,
Loss	4·0 ,,
	100·0

The costs of the process are derived from the following particulars :—

BASIS OF CALCULATION.

Capacity per 24 hours	200,000 litres (44,000 galls.)
Working days per annum	300
Phenol in liquor	0·3 per cent.
Extraction efficiency for phenol	80 ,,
Value of carbolic tar per kg. (2·20 lbs.)	3d.
Wages per shift	15s.
Cost of steam per 1000 kg. (2200 lbs.)	2s.
Electric current per unit	1d.
Cost of plant, including building and foundations	£4000

COSTS.

	£ s. d.	£ s. d.
Income per day—		
Carbolic tar, 480 kg. (1050 lbs.) at 3d.		6 0 0
Expenses per day—		
Steam, 10,000 kg. at 2s.	1 0 0	
Wages, ½ shift at 15s.	0 7 6	
Electricity, 144 units at 1d.	0 12 0	
Sundry expenses	0 2 6	
Amortization at 15 per cent.	2 0 0	
	4 2 0	
Surplus		£1 18 0

Equivalent to 14·25 per cent. on capital.

It should be noted that this estimate of costs does not include loss due to solubility of benzole in liquor and other working losses.

A plant for the recovery of phenols from ammonia liquor is also in operation at the works of Gewerkschaft Stinnes at Karnap, Essen. The following operating figures have been given for this plant (B.P. Nos. 230,705 and 249,111) :—

Ammonia liquor treated per day	125 tons
Phenol content of liquor—	
Crude liquor	0·32 per cent.
After washer No. 1	0·154 ,,
After washer No. 2	0·080 ,,
Extraction efficiency	75 ,,
Phenol content of benzole—	
Recovered benzole	0·09 ,,
After washer No. 1	0·30 ,,
After washer No. 2	1·05 ,,
Composition of crude phenol—	
Phenol	75 ,,
Benzole	15 ,,
Bases	4 ,,
Neutral oil	6 ,,
Composition of phenol (75 per cent. of crude phenol)—	
Carbolic acid	21 ,,
O – cresol	40 ,,
m – cresol	9 ,,
p – cresol and higher phenols	30 ,,

BASIS OF CALCULATION OF COSTS.

Ammonia liquor treated per day	125 tons
Crude benzole employed	31 "
Cost of steam per ton with coal at 10s. per ton	2s. 8d.
Cost of benzole per ton	£14
Cost of power per kilowatt hour	0·54d.
Value of crude phenol per ton	£15 5s.

EXPENDITURE.

	£	s.	d.
Preheating 125 tons liquor to 65° C., 5·5 tons steam	0	14	9
Distillation, 31 tons crude benzole; steam, 7·75 tons	1	1	0
Benzole lost with phenol	0	16	9
Power, 25 kws.	0	1	2
Wages	0	7	0
Depreciation and amortization on £2500	1	0	6
Benzole lost in liquor (0·05 per cent. of liquor)	0	17	6
	£4	18	8

REVENUE.

	£	s.	d.
Phenol (75 per cent.) 0·4 ton	6	2	0
Surplus per day	£1	3	3

Equivalent to 14 per cent. on capital assuming 300 working days per year.

One estimate obtained assumed the value of crude phenol as £12 10s. per ton, in which case the revenue per day would be only £5, leaving only 1s. 2d. as profit instead of 23s. 3d.

The dephenolated liquor at Karnap is afterwards distilled in a concentrated ammonia plant, and any gases, including benzole vaporized from the liquor, are passed back into the coke-oven gas prior to benzole scrubbers. If this procedure could not be adopted, the loss of benzole might be several times the quantity assumed, 0·05 per cent. of the volume of liquor.

Preliminary trials in the laboratory with certain other ammonia liquors gave rise to the formation of troublesome emulsions with benzole. Mention has already been made of similar experience in America.

P. Hoening (Z. Angewandte Chemie, 1929, **42**, 325), in a recent paper describing plants which have been erected in the Emscher district for the recovery of phenols, states that it is preferable to extract the phenols by means of benzole before the ammonia liquor is distilled. The benzole dissolved by the liquor can then be largely recovered by condensation during distillation for the production of concentrated ammonia liquor, or when sulphate is manufactured the vapours containing benzole may be admixed with coke-oven gas prior to the benzole scrubbers. This procedure avoids the contamination of the effluent spent liquors with appreciable quantities of the solvent. It has been suggested that the benzole dissolved by the liquor may be recovered by means of a tar oil or by volatilization in a stream of air or gas and subsequent condensation. Hoening refers to four plants: (1) Dostfeld II/III (Bamag-Meguin A.-G.), (2) König Ludwig (Still), (3) Jakobischächte (Bamag-Meguin A.G.), in consultation with F. Raschig, and (4) Mathias Stinnes I/II (Heinrich Koppers). The fourth plant, Mathias Stinnes I/II, has been in operation since October, 1926, and various methods of operation have been tried. The ammonia liquor is subjected to a preliminary purification from particles of tar by treatment with a limited quantity of benzole in a small washer. The liquor then flows through a heat exchanger, in which its temperature is raised to about 60° C., to the phenol extraction tower. In this tower the liquor flows downwards and meets a stream of benzole flowing in the opposite direction. The phenol may be recovered from the solvent either by distillation or by means of caustic soda followed by acidification. It has been concluded that recovery by caustic soda is the more economical method. The plant has been operated under various conditions to ascertain the influence on the proportion of phenol recovered, of (i.) the volume of solvent employed, (ii.) the temperature of the liquor during treatment with benzole, and (iii.) the nature of the filling in the extraction tower. It was found that of the phenols, carbolic is the last to be removed by benzole since it is the most soluble in the liquor. The extraction is more efficient at 65° C. than at lower temperatures, and perforated trays and 25 mm. Raschig rings were the most satisfactory tower fillings tried.

RECOVERY OF PHENOLS FROM LIQUORS BY SOLID ABSORBENTS.

D. W. Parkes, of Messrs. Robinson Bros., Ltd., West Bromwich (J. Soc. Chem. Ind., 1927, **46**, 186 T.; "Gas Journal," 1927, **179**, 546), has described the results of small scale experiments carried out with the object of recovering phenols from gas liquor effluents by means of activated carbon.

Briefly, the process consists of treating the liquor effluent with carbon dioxide or other reagent until acid to litmus, passing the liquor through a settling tank and then through a series of absorbers containing carbon. The absorbers are cut out in turn, freed from phenols by steam distillation and then returned to circuit. Any carbon lost or rendered inactive is replaced periodically by fresh carbon. A large portion of the tar acids is recovered as liquid tar acids which may be separated by gravity from condensed steam, and a further portion as a 3 per cent. to 4 per cent. solution, which is returned to the absorbers.

It is stated that most of the known commercial carbons and many experimental carbons have been examined. In most instances the carbons are not sufficiently active or the activity decreased rapidly during use in the absorbers. It is claimed, however, that a satisfactory carbon has been procured.

The summarized results of continuous runs with different types of liquor effluents are given in the following table:—

Type.	Phenol Per Cent. in Effluent.	Per Cent. Reduction of Phenol.	Cost of Treatment per Gallon.		
			Cost of Carbon.	Value of Phenols Recovered	Difference.
			d.	d.	d.
A. Mixed	0·38	99·9	0·157	0·045	− 0·112
B. Horizontal	0·24	99·9	0·0224	0·026	+ 0·0036
C. Continuous verticals with steaming	0·14	99·3	0·127	0·005	− 0·122
F. Continuous verticals with steaming	0·407	99·5	0·0884	0·045	− 0·0434

The costs given in this table refer only to the carbon used and the phenol recovered, and give no indication of operating and other costs on a commercial scale. H. W. Robinson and D. W. Parkes (B.P. 305,494) have also proposed the removal of higher tar acids for the recovery of catechol from gas liquor effluents by means of lead chloride and other compounds as a preliminary to the activated carbon process. Further investigation is required before an opinion could be given as to the possibilities of development of the process as a reliable large scale operation.

REMOVAL OF PHENOLS BY VOLATILIZATION.

By the passage of steam and hot flue gases through spent liquor, provided the temperature of the liquor be maintained above 90° C., the colour can in many instances be removed, and at the same time a considerable portion of the phenols (ordinarily determined as C_6H_5OH—*i.e.*, not including higher tar acids) can be volatilized.

Dr. T. L. Bailey (Reports of Chief Inspector of Alkali Works, 1920 to 1927) has carried out a number of small and large scale experiments in collaboration with the authorities of several gas-works, including Bolton, Hornsey, Leamington, Macclesfield, and Stockport. The process consists of causing effluent liquor to flow through suitably packed towers or through troughs provided with supplies of steam and chimney gases. The phenols removed are not recovered, but are allowed to escape into the atmosphere. At Hornsey, where dephenolating towers have dealt with the whole of the effluent liquors produced in the manufacture of 2½ to 3 tons of sulphate of ammonia per day, analyses indicated a volatilization of over 70 per cent. of the phenols, and another plant has achieved a continuous removal of more than 90 per cent.

The process, however, is costly in steam, one installation requiring an amount of steam equivalent to approximately 36 per cent. of the weight of effluent treated; and separation of solid matter on the packing of the dephenolating tower has given trouble in some instances. With the object of reducing steam consumption, experiments

have been carried out at a works in the Midlands, where an open dephenolating trough was installed in a hot gas flue. The effluent liquor was made to flow through the trough, which was fitted with steam coil and a perforated pipe for the injection of chimney gases or air under controlled conditions. The project has, however, been abandoned.

L. W. Heffner and W. Tiddy (B.P. 244,774 and 244,775) state that if gas liquor, before or during its passage through the preheaters and free ammonia sections of an ammonia still, be heated to a minimum temperature of 98° C. in presence of a sufficient quantity of free ammonia, most of the phenol is volatilized. The phenol is separated by passing the combined vapours through a washer containing lime, caustic soda, absorbent carbon, or other medium for the removal of phenol and tar acids. The inventors claim that ammonium phenolates are more volatile than the phenols themselves, and state that if the ammonia content of the liquor is low they provide additional ammonia prior to distillation. Dr. Bailey has carried out laboratory experiments to determine the effect on the rate of volatilization of phenol, of increasing the ammonia content of a given liquor from *nil* to 6 per cent., but found that the addition of ammonia had little effect; in fact, the maximum amount of phenol volatilized was obtained in absence of ammonia.

When ammonia liquor is distilled by usual processes, a large proportion of the phenol—in some cases as much as 40 per cent.—is volatilized with the ammonia and condenses with the devil liquor. Several gas-works have successfully evaporated devil liquor by injecting it vertically upwards in the form of an atomized spray in the base of a hot boiler-house or retort-house chimney.

The Koppers Company process,* particulars of which were kindly supplied by Dr. E. W. Smith, consists of taking the hot ammoniacal liquor from the bottom of the "free" still (when it is completely free from free ammonia, carbon dioxide, and sulphuretted hydrogen), and pumping it to the top of a dephenolizing tower, which is packed with spiral rings. In its passage through this tower, the tar acids are removed and the liquor containing fixed ammonia compounds passes back into the "fixed" still. In the dephenolizing tower, the liquor meets hot steam and waste gas, the proportion of steam being over 90 per cent. of the circulating vapours. The circulating vapours are in a closed cycle, being circulated by means of a fan. Vapours containing phenol are drawn from the top of the tower and pass through three towers packed with steel turnings. In these three towers the vapours meet a 10 per cent. solution of caustic soda which decants from the top to the bottom. The solution employed in the second and third towers is recirculated continuously, but the caustic soda is added to No. 1 tower in batches every half-hour. There are steam coils in the second and third towers to maintain the temperature of the system such that neither evaporation nor condensation occurs.

For each gallon of waste liquor dephenolized there are circulated 400 c.ft. of steam vapour mixture at 100° C. At the Hamilton Coke and Iron Company, the dephenolizing tower is 7 ft. in diameter and 90 ft. in total height, and is lagged from top to bottom.

The sodium phenolate solution leaving the plant is used for washing benzole on the pure benzole plant. After the acid wash, the benzole is treated with sodium phenolate in two stages. In the first wash, insufficient sodium phenolate is added completely to neutralize the acid. Some phenol is dissolved by the benzole, but the sodium sulphate, &c., can be run off with the wash liquor. In the second wash, an excess of sodium phenolate is added, which causes the phenol dissolved in the benzole to be washed out by means of the excess soda in the sodium phenolate. The sodium phenolate containing less free soda as the result of its use in the benzole plant, is then treated with stack gases, and the acid constituents cause

* Since this memorandum was prepared, a description by B. F. Hatch of the Koppers process has been published; Indust. Eng. Chem., 1929, **21**, 5 and 431; Gas J., 1929, **187**, 407.

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the phenol to be liberated and sodium carbonate to be formed.

In America this sodium carbonate solution is available for liquid purification, or, alternatively is used for boiler feed water. The phenol is either sold as crude phenol or distilled to make pure phenol.

EXTRACTION OF PHENOLS FROM CRUDE GAS AT TEMPERATURES ABOVE THE DEW-POINT OF THE GAS.

The methods so far described in this memorandum have been devised with the object of removing and in many cases recovering the phenols present in ammonia liquor and effluent liquors. The question arises as to whether it is possible so to modify conditions in gas manufacture as to avoid the initial contamination of ammonia liquor by phenols. It has already been proved (Second Report of Effluents Committee) that the proportion of the less volatile higher tar acids in liquor can be reduced by methods of deposition of heavy tar from the hot gas at temperatures above the dew-point, before the condensation of liquor commences. It may also be possible to remove large proportions of the more volatile monohydric phenols from the hot gas before condensation of liquor occurs, by the use of suitable scrubbing agents or other media.* This problem would appear to be worthy of systematic investigation.

In conclusion, it should be mentioned that this account of the processes devised and suggested for the removal of phenols from ammoniacal liquors and spent gas liquor is not intended to be exhaustive, but to describe typical processes illustrative of general principles. The list of references which follows includes the more important papers consulted in the preparation of the memorandum.

An abstract translation of a report by M. Prüss on Effluents and the Phenol Problem was reproduced as an appendix. This was reprinted from the "JOURNAL" for Aug. 21, 1929.

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* Since this memorandum was prepared, an account has appeared in the "GAS JOURNAL," Oct. 23, 1929, p. 251, of a method proposed by the Manchester Oxide Company and R. H. Clayton (E.P.319,382) for the removal of tar fog and monohydric phenols from hot crude coal gas.

REPORT ON A VISIT TO GERMANY TO INSPECT THE METHODS ADOPTED FOR THE RECOVERY OF PHENOLS FROM AMMONIA LIQUORS AND KINDRED SUBJECTS.

By ALLAN C. MONKHOUSE, Ph.D., B.Sc., A.I.C.
(Research Chemist).

INTRODUCTION.

Owing to the concentration of collieries and coke ovens in the Ruhr district, the question of the disposal of waste liquors is a very vital one to which considerable attention has been given in Germany.

The Emschergenossenschaft, founded in 1904, is an organization representing the towns, districts, and manufacturers, and controlling an area of some 300 sq. miles, drained by the Emscher, a tributary of the Rhine. Its object is the disposal of waste waters in that area, and much work has been done in the building of sedimentation works, drainage, and canalization. The Emschergenossenschaft has in its area about 90 coke ovens, carbonizing 20 million tons of coal per annum. In view of the pollution of the waters with phenol, a Commission was appointed to investigate the problem. Both biological and solvent methods were considered in detail and large-scale plants erected. The patent rights for the area for washing the liquor with solvents to remove the phenol were purchased by the Association. At the present time four phenol plants are in operation and six in course of construction.

A similar association—the Ruhrverband—founded in 1913, deals with the water from another area in which are carbonized 1·5 million tons of coal per annum.

It is estimated that in the Ruhr district, where 35 to 40 million tons of coal are coked per annum, the phenols recoverable from the waste liquors amount to 25,000 to 30,000 tons per annum. The present demand for phenols in Germany is 11,000 tons per annum. An increasing amount is required for the manufacture of such products as Bakelite, &c., and new uses for phenols are being investigated in Germany.

1. PHENOL RECOVERY FROM AMMONIA LIQUORS BY MEANS OF SOLVENTS.

The general principles of the methods adopted for the recovery of phenols from ammonia liquors are—

1. A preliminary washing or filtration of the ammonia liquor to remove tarry particles.
2. The washing of the ammonia with (*a*) benzole or (*b*) tar oils in a suitable washer, static or rotary, for the removal of the phenols.
3. The recovery of the phenols from the washing liquid, (*a*) as crude phenols by distillation or (*b*) as sodium phenolate solution by washing with soda solution.

A detailed description of particular plants in operation or in course of construction is appended.

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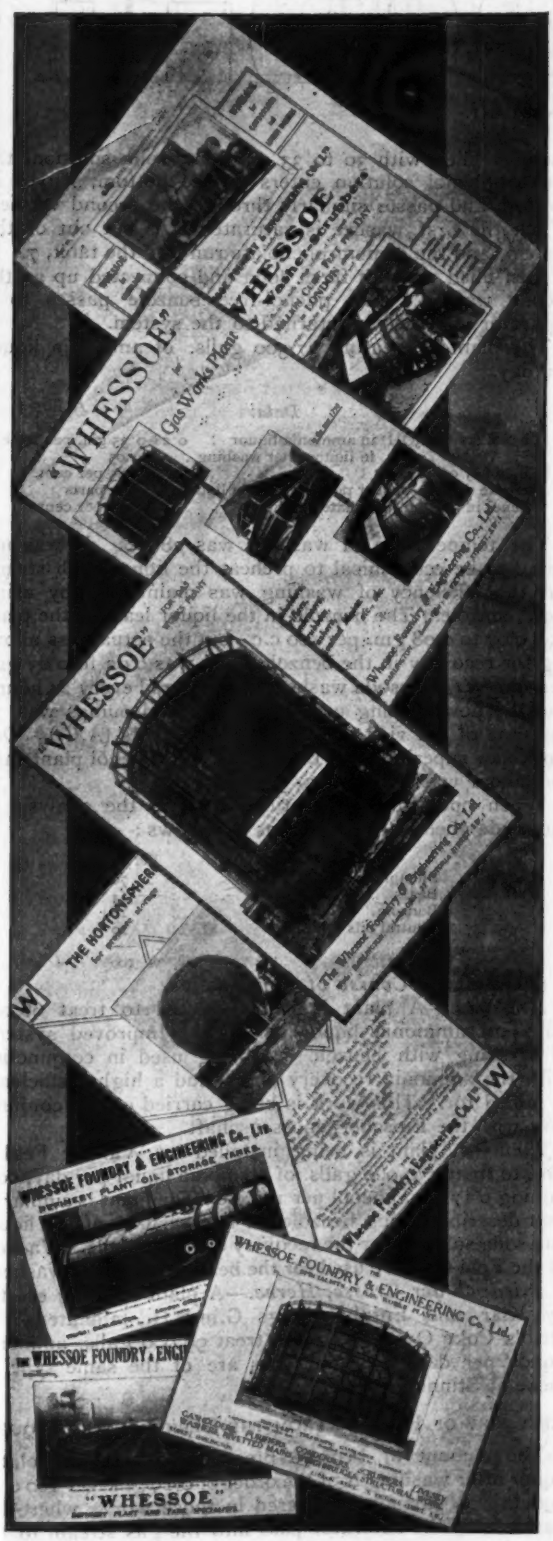

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(*a*) *Jacobischächte.*—Plant erected by Bamag-Meguin A.-G., in consultation with Dr. Raschig.

Principle: 1. Washing the liquor with benzole in a washer filled with Raschig rings.

2. Recovery of the crude phenols by distillation.

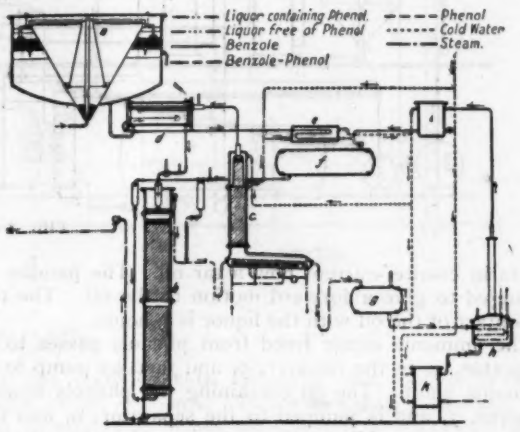

FIG. 1.—JACOBISCHÄCHTE PLANT.

The diagram of the plant is shown in Fig. 1. After the removal of tarry particles in a filter, *a*, the ammonia liquor flows through the preheater, *d*, to the scrubber, *b*, filled with Raschig rings, and thence to the ammonia distillation plant. Benzole enters at the bottom of the scrubber, and the benzole enriched with phenol flows to the still, *c*, where the benzole is distilled from the phenols by indirect steam. The vapours pass through the tall column filled with Raschig rings, are cooled by passage through the ammonia liquor preheater, *d*, and the cooler, *e*. The condensed benzole flows to the storage tank, *f*. The crude phenols leave the bottom of the still and flow to container, *g*, and can be freed from the last traces of benzole in the still, *h*. The benzole left in the ammonia liquor is partially recovered as the indirect process of ammonia recovery is used with subsequent removal of benzole from the gas stream.

The plant has been in operation for 2½ years, and is capable of treating 33,000 galls of ammonia liquor per day. The plant occupies an area of 27 ft. by 12 ft., and a maximum height of 56 ft.

Data.

Average phenol content of ammonia liquor . .	0·45 gm. per 100 c.c.
,, ,, ,, ,, liquor after washing .	0·16 ,, ,, ,,
Efficiency of washing	65 per cent.
Crude phenols obtained per ton of coal carbonized (average)	1·5 lbs.
Phenol content of crude phenols	63 per cent.
Benzole used as percentage of the ammonia liquor	35 ,,
Benzole loss per lb. of crude phenols obtained .	0·25 lb.
,, ,, per 100 galls. of ammonia liquor .	0·65 ,,
Steam consumption per lb. of crude phenol . .	20 lbs.

The benzole used in the washing process is about 35 per cent. of the volume of the liquor. It was found that when the plant was working with a low throughput—*i.e.*, a longer time contact, more of the phenol (C_6H_5OH) was extracted from the liquor, and a correspondingly better price obtained for the crude phenols. The optimum temperature for washing the ammonia liquor was found to be 60° C. A preliminary removal of tarry particles is essential or emulsions are formed in the later stages. The temperature of the crude phenols leaving the bottom of the still is 150° C., and the phenols contain 3 to 5 per cent. of benzole.

(*b*) *Vondern.*—Plant erected by Bamag-Meguin A.-G.

Principle: 1. Washing the liquor with tar oil.

2. Recovery of the phenols as sodium phenolate solution using soda solution.

The diagram of the plant is shown in Fig. 2. The ammonia liquor is first freed from tarry particles in filter, 1, and then passes through the preheater, 2, to the trough washer, 3, containing rotating paddles in which the liquor

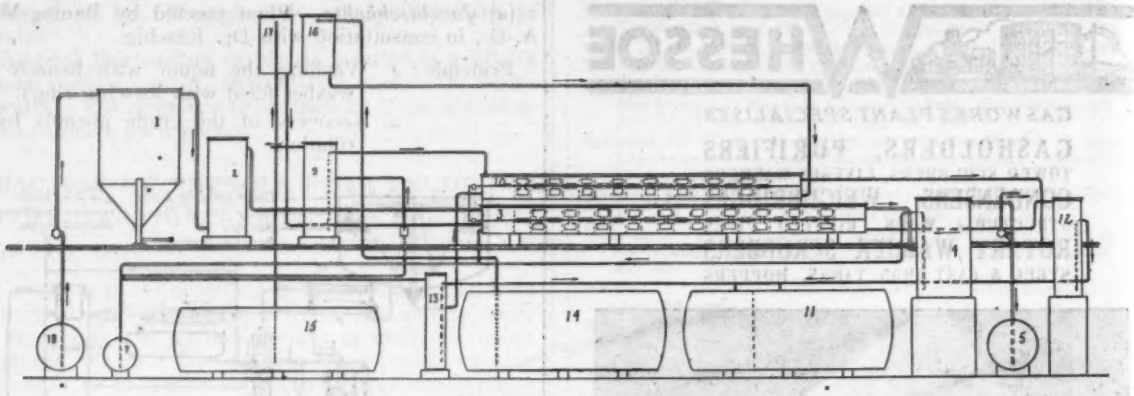

FIG. 2.—VONDERN PLANT.

meets in counter-current flow a tar oil. The paddles are arranged to give a forward motion to the oil. The time of contact of the oil with the liquor is 3 hours.

The ammonia liquor freed from phenols passes to the separator, 4, to the receiver, 5, and then by pump to the ammonia plant. The oil containing the phenols flows to receiver, 7, and is pumped to the separator, 9, and then to the second paddle washer, 10, in which the oil meets the soda solution in counter-current flow. The dephenolated oil returns to the washer, 3, and the sodium phenolate solution to tank, 11, both solutions passing through the separators, 12 and 13, respectively. Fresh soda and oil are elevated by compressed air to tank, 16, and tank, 17, and from there flow to the washers. The plant has been in operation since November, 1928, and is treating 22,000 galls. of ammonia liquor per day.

Data.

Phenol (as C_6H_5OH) in ammonia liquor	0·34 gm. per 100 c.c.
,, ,, in liquor after washing	0·04 ,, ,, ,,
Efficiency of washing	88 per cent.
Phenol content of sodium phenolate solution	25 ,,

The early experiments using tar oil as a washing medium were made in one paddle washer having three layers—ammonia liquor, oil, and soda, but owing to the formation of emulsions this system was abandoned. The tar oil used is free from naphthalene, and has a boiling range 230° to 270° C. Small amounts of emulsion are obtained in the existing plant in the oil-soda washing, but these are broken down in a separate vessel using sulphuric acid. The speed of rotation of the paddles is 12 revs. per minute.

(*c*) *Zeche Dorstfeld 2/3. Henrichshütte, Hattingen.* } Erected by Bamag Meguin A.-G.

These plants differ from the Jacobischächte plant in that the benzole and ammonia liquor are mixed in a centrifugal pump or pumps. This method does not appear to be quite as satisfactory as the counter-current column washer, due to the shorter time of contact, and tendency to emulsification.

(*d*) *Stinnes I/II.*—Plant erected by Heinrich Koppers A.-G.

Principle: (1) Washing the ammonia liquor with benzole.

(2) Recovery of the phenols (*a*) by distillation; (*b*) by soda solution.

The plant when visited was only operating the recovery of phenols by the soda solution method, but plant was available for the distillation of the benzole-phenol solution if desired. This method of recovery had been used, but the soda method was found to be more economical.

The diagram of the plant is shown in Fig. 3. The ammonia liquor passes through a tar washer, 1, half filled with benzole. This benzole remains in the washer until saturated with tar. The liquor is then pumped to the phenol washer, 2, consisting of a number of sections with sieves where it meets an upflowing stream of benzole. The dephenolated liquor flows to the separator, 3, and then to the ammonia plant. The benzole enriched with phenol flows through the separator, 4, in which any ammonia liquor is removed to the soda washers, 5 and 6. This process is worked intermittently. The washers are partially filled with 30 to 33 per cent. soda solution, the benzole-phenol solution enters at the bottom, leaves at the top, and passes similarly through the second washer. When the first washer is saturated it is cut out of the system, and the sodium phenolate run into the tank, 7. It is then filled up with fresh soda and connected up as the second washer. The phenol-free benzole passes to a separator and then is returned to the system.

The plant is treating 27,500 galls. of ammonia liquor per day.

Data.

Phenol (as C_6H_5OH) in ammonia liquor	0·28–0·35 gm. per 100 c.c.
,, ,, in liquor after washing	0·05 ,, ,, ,,
Efficiency of washing	85 per cent.
Benzole used in washer per 100 parts of liquor	77 parts
Phenol in sodium phenolate solution	26–27 per cent.

The temperature of washing was 28° C. It was not found to be economical to preheat the liquor with steam, but the efficiency of washing was maintained by using more benzole. The benzole in the liquor leaving the plant was 0·07 to 0·08 gm. per 100 c.c., but the actual loss allowing for recovery in the benzole plant was 0·02 to 0·03 gm. per 100 c.c. The soda washers are changed every 24 hours, and the power being used for stirrer and pumps was, at the time of the visit, 16 amps. at 220 volts (A.C.). One workman superintended the benzole and phenol plant, and the labour was reckoned at ½ man per shift.

When operating the distillation plant the analysis of the crude phenols obtained was as follows:—

	Per Cent.
Phenols	70
Bases	4
Benzole	16
Neutral oils	10
	100

(*e*) *Plants in Course of Construction.*

Mansfeld.—A plant is being erected to treat 66,000 galls. of ammonia liquor per day. Improved systems of washing with benzole are being used in conjunction with the ammonia recovery plant, and a higher efficiency is hoped for. This work is being carried out in conjunction with the Emschergenossenschaft.

Emil.—A plant is being installed by Walther Feld & Co., to treat 130,000 galls. of ammonia liquor per day, containing 0·17 gm. phenol per 100 c.c. The plant is similar to that described using benzole for the washing of the liquor and soda solution for the recovery of the phenols. Washers of the Feld type are used for the benzole and soda washers.

Friedrich der Grosse, Herne.—A plant is being erected by Klär und Entphenolungs G.m.b.H. (affiliated with Otto's Coke Ovens, Ltd.) to treat 99,000 galls. ammonia liquor per day. The washers are of the same type as those at Stinnes I/II.

RECOVERY OF BENZOLE FROM THE DEPHENOLATED LIQUOR.

The amount of benzole present in the dephenolated liquor after washing is of the order of 0·15 gm. per 100 c.c., and this is partially recovered in those works where the gases from the saturator pass into the gas stream to the benzole recovery plant. In works where concentrated ammonia liquor is made, the benzole separates out as a layer and can be recovered.

Experiments have been made at Stinnes I/II in washing

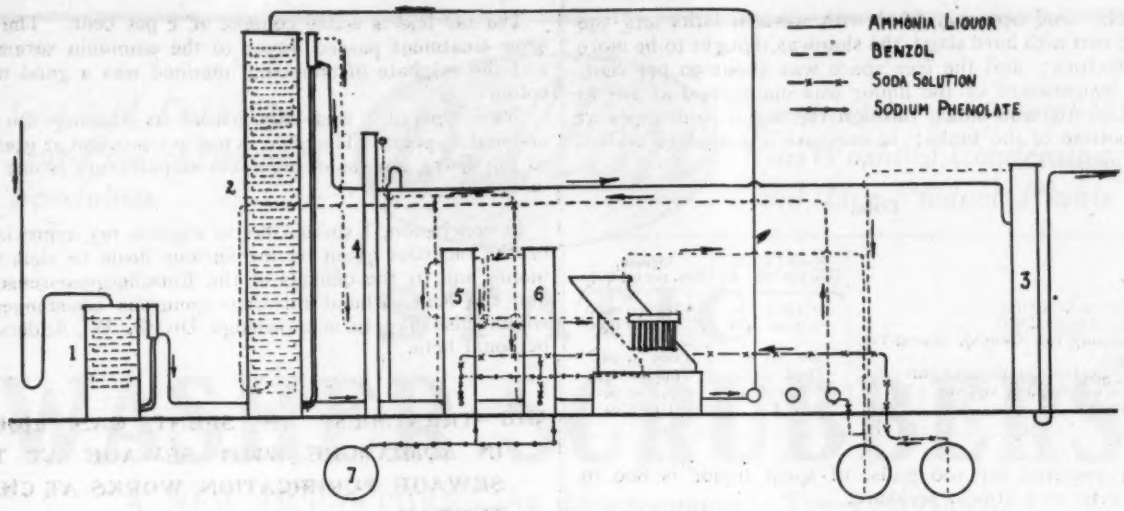

FIG. 3.—STINNES I/II PLANT.

the dephenolated liquor with Rivasol—a brown coal tar oil—which can be enriched up to 10 per cent. with benzole, and the benzole in the liquor reduced to 0·05 gm. per 100 c.c.

At Dorstfeld, air is blown through the liquor at 75° C., and the benzole condensed from the gas by cooling. The benzole in the liquor is reduced to 0·01 to 0·03 gm. per 100 c.c.

A Comparison of the Solvent Methods of Phenol Recovery.

Benzole is the more common solvent since greater difficulties have been experienced with emulsions when heavy tar oil is used, although it is claimed that these difficulties have been successfully overcome. An important factor is a satisfactory removal of tarry particles before washing with the solvent. The advantages of tar oil are its lower solubility in the ammonia liquor, its cheaper cost, and lower volatility.

The efficiency of washing using benzole depends on the temperature of washing, the proportion of benzole, and the type of washer used. The phenols may be recovered from the benzole as crude phenols by distillation or as sodium phenolate solution using soda washing. The advantages of the distillation method are :—

1. Less plant area.
2. Lower carriage costs for the crude phenols.
3. Waste heat available for heating the liquor.

The advantages of the soda method are :—

1. No steam required.
2. A larger volume of benzole can be used (due to there being no subsequent distillation costs to be considered), with an improved washing efficiency. It should be mentioned that the most valuable phenol —carbolic acid—is less easily removed from the liquor than the cresols, and an increased efficiency of washing means an increased proportion of carbolic acid.
3. There is no loss of benzole in the final product comparable with that in distillation, in which the amount of benzole may amount to 14 per cent. by volume.

Costs given by P. Hoening, of Mathias Stinnes I/II, where the two processes were tried are as follows :—

	Distillation Method.	Soda Washing.
Cost per ton of phenols . . .	£14 ..	£8 16s.

In the distillation method the loss of benzole in the crude phenols was equivalent to £3, and the steam for distillation to £4 per ton of phenol.

The capital cost of a phenol recovery plant treating 33,000 galls. of ammonia liquor per day is on the average £3000, and it was stated that, assuming the prices then holding of 2d. per lb. for crude phenols, the plant would pay for itself in three years.

It was considered in Germany that phenol recovery cannot be an economic success for plants treating less than 10,000 galls. of ammonia liquor per day, equivalent to a 1000 million works. The types of large-scale plant at present in operation in Germany are in general those on which alterations and experiments have been made. In every case success has been attained, and new plants are being erected embodying the latest principles of design and lay-out. It is not possible at this stage to form a decision as to the best type of plant, but the results of the working of the new plants at the end of the year should yield useful information.

II. THE RECOVERY OF PHENOLS BY MEANS OF ACTIVE CARBON.

The Lurgi G.m.b.H. have carried out experimental work on the recovery of phenols using active carbon, and as a result of their experiments are erecting a large-scale plant. The ammonia liquor, after removal of tarry matter, is passed through active carbon, and the phenol is subsequently recovered by washing the carbon with benzole.

III. BACTERIAL PURIFICATION.

The work of Fowler and his collaborators has been applied by Dr. Bach, of the Emschergenossenschaft, to the purification of coke oven effluents. Dr. Bach has modified the practice of percolating filters, and employs "Emscher" filters. The plant consists of a tank filled with media, such as hard slag or wooden laths. Diluted spent liquor is led by circuitous path down and up the tank, and at the same time air is bubbled through the liquid from air pipes placed at the bottom. The media is first activated with domestic sewage or dung. Spent liquor is then added in increasing proportions, and eventually spent liquor is diluted with purified effluent. It is recommended, however, that a small amount of domestic sewage be continually added to the feed liquor. The following results are claimed in comparison with the percolating filter method :—

Method.	Trickling Filter.	Compressed Air. Aerated Contact Bed.
Dilution of spent liquor .	1 : 9	1 : 3
Aeration time	..	3 hours
Water capacity of media	..	50 vols. per cent.
Vol. treated per cub. yard of media per day . .	100 galls. of diluted liquor, or 10 galls. of spent liquor	673 galls. of diluted liquor, or 168 galls. of spent liquor
1 ton of $(NH_4)_2SO_4$ equiv. to 3960 galls. of spent liquor per day requires	392 cub. yards of media	24 cub. yards of media

An experimental plant at the Coke Ovens, Helene, Essen, was visited. The plant was treating 220 galls. of spent liquor per hour, and the degree of dilution in use was one part crude liquor to three parts of purified effluent, together with a small flow of domestic sewage from the

works. One bed was filled with wooden laths and the other two with hard slag; the slag was thought to be more satisfactory; and the free space was about 50 per cent. The temperature of the liquor was maintained at 26° to 28° C. Air was blown through the liquid from pipes at the bottom of the tanks; in one case a pendulum system was adopted.

Data.

—	Spent Liquor. Gm. per 100 C.C.	Effluent. Gm. per 100 C.C.
Phenols (as C_6H_5OH)	0·130–0·210	0·0015–0·0040
Thiocyanate (as CNS)	0·010–0·016	0–0·0006
Oxidizability (as $KMnO_4$), (Kubel-Tiemann)	1·1 –3·8	0·065 –0·085
Biochemical oxygen requirements	Over 0·1	Under 0·01
Organic and sulphide sulphur	0·030–0·045	0·001 –0·002
Toxicity	1	1/18–1/40

Air required for 100 galls. of spent liquor is 800 to 1300 c.ft. at ½ atmos. pressure.

Sludge is run out from the bottom of the tanks once a month. The cost of treatment is 1·6d. to 2·7d. per 100 galls. of spent liquor.

A second plant was visited at Mansfeld in the Ruhrverband district, treating 22,000 to 26,000 galls. per day. The spent liquor, containing 0·15 gm. phenol per 100 c.c., after passing through settling tanks, was diluted in the proportion of 3 to 5 with domestic sewage. The liquid passed first through an "Emscher" filter and then through an activated sludge tank. The time of contact in the Emscher filter was 1½ hours and in the activated sludge tank 2 hours. In the Emscher filter one-third of the phenols was removed, and in the activated sludge tank two-thirds. The Emscher filter was filled with wooden laths, and the pendulum system of aeration was used. The total air used was approximately 880 c.ft. per 100 galls. of crude liquor treated. The power costs for air were given as 0·3d. per 100 galls. treated.

IV. THE TREATMENT OF COLLIERY AND COKE OVEN WASTES AT KARNAP.

A sludge settling works has been erected at Karnap, consisting of 4 settling tanks treating the whole of the River Emscher, a volume of 290 to 570 million galls. per day. The amount of sludge obtained per day is 440,000 galls. The water entering is dark, oily, phenolic in smell, and containing a very high percentage of solid matter. The plant commenced operation in January, 1929. A central electricity generating station is to be erected in the neighbourhood to burn the dried sludge obtained.

V. ELECTROSTATIC TAR PRECIPITATION.

Two firms were exhibiting working models of precipitation plants at the Exhibition, using disc rectification—Lurgi Apparatebau G.m.b.H. and Siemens-Schuckertwerke A.-G. Plants are in operation on tar removal from water gas plants and brown coal generators. A plant had been in operation at Osterfeld on coke oven gas, and the following data were obtained from Lurgi G.m.b.H. :—

Plant at Osterfeld.

Gas treated	2·5 million c.ft. per day
Temperature of gas	80°–90° C.
Power consumption per 1000 c.ft. of gas	0·04 kilowatt-hour

The tar fog content of the purified gas under different conditions was as follows :—

C.Ft. of Gas per Hour at 80° C.	Load Per Cent.	Tar Content. Grains per 100 C.Ft. 0°C.
176,000	17 under	2·3
212,000	Normal	2·7
247,000	17 over	6·1

The tar had a water content of 1 per cent. The gas after treatment passed direct to the ammonia saturator, and the sulphate of ammonia obtained was a good white colour.

Some difficulty was experienced in keeping the gas above dew-point. The plant is not in operation at present, as the direct process of ammonia manufacture is not now in use.

In conclusion, I should like to express my appreciation of the facilities given by the various firms to visit their plants and to the officials of the Emschergenossenschaft and the Ruhrverband for their generous assistance. I should also like to acknowledge Dr. G. W. Anderson's personal help.

THE TREATMENT OF SPENT GAS LIQUOR IN ADMIXTURE WITH SEWAGE AT THE SEWAGE PURIFICATION WORKS AT CHELTENHAM.

This paper consists of a summary prepared by Dr. A. C. Monkhouse of a Report made by Mr. F. R. O'Shaughnessy, A.R.S.C., F.I.C., for the Cheltenham Gas Light and Coke Company and is published through the kind permission of the Directors of the Company, Mr. L. E. Twycross (Engineer), the Cheltenham Corporation, Mr. J. S. Pickering, M.Inst.C.E. (Borough Engineer), and Mr. F. R. O'Shaughnessy.

Introduction.—The treatment of spent liquor in admixture with sewage has already been investigated in detail by several workers as described in the Reports of the Royal Commission on Sewage Disposal and the preceding reports of the Liquor Effluents Sub-Committee. The influence of the admission of spent liquor to the sewers and detailed observation of its effect on the purification at the sewage works over a considerable period has however not been recorded. The particular case described is one in which observations were made on the addition of spent gas liquor from vertical retorts to a domestic sewage in which no other trade waste was present, thus providing an ideal case for observation.

DESCRIPTION OF PLANT.

The Gas-Works.—The carbonizing plant at Cheltenham consists of a vertical retort house, with a capacity of 1½ million cubic feet per day, and a horizontal house, with a capacity of 1¾ million cubic feet per day. During the earlier period of the tests the vertical retorts only were in operation.

The sulphate plant is of 2-ton capacity per day. The "free" ammonia only is recovered, no lime being added to the still. The spent liquor from the still flows to an underground tank of 180,000 gallons capacity from which it is pumped to an elevated service tank, and thence through a V-notch Palatine recorder to the sewers.

The coal carbonized per annum is 40,000 tons, and the make of spent liquor is 2 million gallons per annum.

The Sewage Works.—The sewage purification works at Cheltenham at which the spent gas liquor is treated consists of detritus tanks, sedimentation tanks, and percolating filters. The sedimentation tanks are twelve in number and of circular shape, connected to give three parallel streams of sewage, the nominal time of retention in these being 18 hours. The tank effluent flows to gauging chambers and thence to the percolating filters. The rate of flow is thus accurately controlled and is of the order of 110 gallons per cube yard per day. The bacteria beds are 101 ft. diameter, 4 ft. 6 in. deep, filtted with granite of 1½ in. grade, the top 8 in. being ¾ in. grade. The effluent from the beds after settlement of humus is discharged.

The dry weather flow of sewage per day is 1,750,000 gallons, and the average proportion of spent gas liquor during the year is 0·3 per cent. of the dry weather flow.

Summary of Investigation.—The crude sewage settling tank effluent, and final effluent at the sewage works was first examined when no spent liquor was being admitted to the sewers. The tests were made over a period of 14 days in May, 1927. No samples were taken on wet days.

The sampling was done every hour over this period, the

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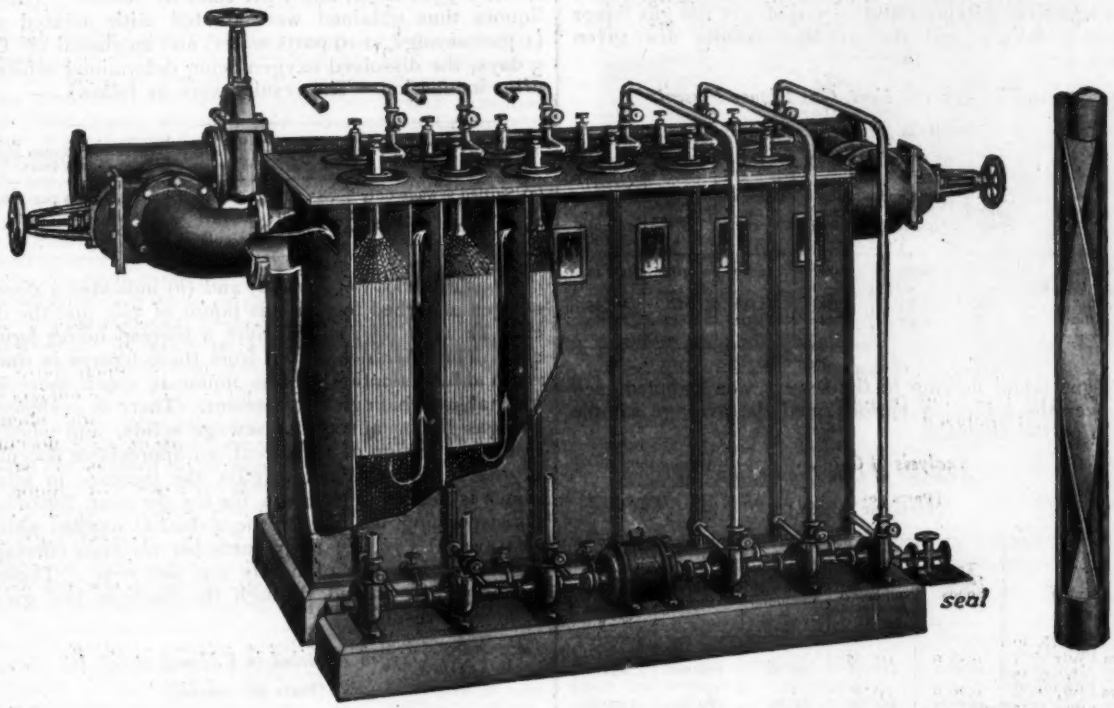

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24 samples at each point being mixed to give the average sample for the day, and these samples were then analyzed.

The average results for the 14 days were as follows :—

STAGE I.—*No Gas Liquor Present.*

[Results in parts per 100,000.]

Description.	Suspended Solids.	Free and Saline Ammonia.	Albuminoid Ammonia.	Chlorine as Chlorides.	Oxidized Nitrogen.	Oxygen Absorbed in 4 Hours. 80° F.
Crude sewage .	16·00	4·34	0·62	9·33	*nil*	5·47
Settling tank effluent . .	2·60	4·74	0·48	9·59	*nil*	3·76
Final effluent .	2·16	0·32	0·07	9·36	2·14	1·14

The results indicate that the Cheltenham sewage (without gas liquor present) is a weak domestic sewage, fairly regular in character during dry weather. Also, the preliminary tank treatment is very effective, and the final effluent from the works is of good quality, being well aerated, non-putrefactive, and complying with the Royal Commission Standard. The percentage purification on the 4 hr. oxygen absorbed basis lay between 80 per cent. and 90 per cent.

The influence of gas liquor in the proportion of 0·5 per cent. of the dry weather flow of sewage was next investigated. Liquor from the spent liquor storage tank at the gas-works was admitted to the sewers at a constant rate through a V-notch recorder in the desired proportion, and after an interval of 24 hours sampling at the sewage works was started. The discharge of spent liquor commenced on July 16, 1927, and sampling of the crude sewage tank effluent, and final effluent was carried out as previously described up to July 27 (except on July 21, which was wet). Representative samples of the gas liquor were also taken, and the average results are given below :—

STAGE II.—0·5 *Per Cent. Gas Liquor Present.*

[Results in parts per 100,000.]

Description.	Suspended Solids.	Free and Saline Ammonia.	Albuminoid Ammonia.	Chlorine as Chlorides.	Oxidized Nitrogen.	Oxygen Absorbed in 4 Hours. 80° F.
Crude sewage .	19·00	6·85	0·90	14·60	*nil*	13·49
Settling tank effluent . .	3·60	6·88	0·61	14·48	*nil*	10·55
Final effluent .	1·86	1·73	0·13	13·02	2·42	1·60

The gas liquor flowing to the sewers was sampled each hour over the following periods, and the average sample of each period analyzed.

Analysis of Gas Liquor.

[Parts per 100,000.]

Description.	Total Solids.	Free and Saline Ammonia.	Albuminoid Ammonia.	Alkalinity as $CaCO_3$.	Oxygen Absorbed in 4 Hours. 80° F.
8 a.m., July 16, to 8 a.m., July 18 .	1616·0	441·35	30·29	120·0	1291·6
6 p.m., July 19, to 2 p.m., July 21 .	1926·0	452·60	22·80	180·0	1370·8
4 p.m., July 24, to 4 p.m., July 25 .	1736·0	512·60	34·00	160·0	1479·0
3 p.m., July 26, to 3 p.m., July 28 .	1516·0	473·60	21·10	160·0	1333·3
Average . .	1698·5	470·04	27·05	155·0	1368·7

An average sample of the above gave the following analysis :—

Phenols	307·1 parts per 100,000
Thiocyanate (CNS)	444·0 " " "
Sulphur as thiosulphate . . .	56·3 " " "

The waste gas liquor is very strong due to the liquor being from vertical retorts only and less dilution due to the " fixed " ammonia not being recovered. The increase in the figures obtained on analyzing the sewage agree very well with the calculated amounts due to 0·5 per cent. of spent gas liquor.

The sewage is converted on the basis of the oxygen absorbed figures, from a sewage of " weak " to one of " average " strength.

Practically all the samples of sewage containing gas liquor remained inoffensive whilst standing in the laboratory. Thus gas liquor would help to keep down offensive odours both in the sewers and while passing through the settling tanks. The odour of the gas liquor could be detected in the sewage. The final effluent remained bright with an increase in the oxidized nitrogen due to the larger amount of ammonia in the sewage. All the samples were non-putrefactive, and the Royal Commission test gave satisfactory results.

The gas liquor was maintained at the above strength for three weeks when slightly weaker stocks were used for a further three weeks. The bacteria beds were kept under close observation during the whole period, and the condition of the beds was not impaired, and the life therein remained vigorous and healthy.

Experiments were also carried out with a 1 per cent. flow of spent liquor on the dry weather flow of sewage, the average strength of the liquor in terms of oxygen absorbed at 4 hours being 1265·8 parts per 100,000. Owing to the rainy season during which the tests were conducted and the lower strength of the spent gas liquor the average analysis of the crude sewage was a little less than the figures already given. The final effluents were non-putrefactive, well aerated, and complied with the Royal Commission Standard.

Laboratory experiments were made on the relative " facility of treatment " of spent gas liquor by biological oxidation. An average sample of the gas liquor was added to the settled tank liquor in the proportion of 0·0 per cent., 0·5 per cent., and 1 per cent. by volume. The three liquors thus obtained were diluted with aerated water (1 part sewage to 19 parts water) and incubated 18° C. for 5 days, the dissolved oxygen being determined before and after incubation. The results were as follows :—

—	Dissolved Oxygen Absorbed in 5 Days.
(*a*) Settled sewage only	8·84 parts per 100,000
(*b*) " " + 0·5 per cent. gas liquor.	11·44 " " "
(*c*) " " + 1·0 " " " .	12·64 " " "

The difference between (*a*) and (*b*) indicates a dissolved oxygen absorbed for the gas liquor of 520, and the difference between (*b*) and (*c*) gives a corresponding figure of 240. The inference drawn from these figures is that the more dilute solution of gas liquor is much more easily amenable to biological treatment. There is evidence that the gas liquor affects the sewage solids, and when it is in the proportion of 1 per cent. an appreciable flocculation of these solids occurs. Again the increase in strength above is nearly 30 per cent. for 0·5 per cent. liquor. The corresponding figures for the 4 hours' oxygen absorbed test are (*a*) 3·76, (*b*) 10·55 parts per 100,000, corresponding to an increase of nearly 200 per cent. These two liquors when passed through the bacteria bed give the following results :—

Oxygen Absorbed in 4 Hours at 80° F.

[Parts per 100,000.]

No gas liquor present	1·14
0·5 per cent. gas liquor present	1·60
Difference between the two sewage figures	6·79 parts per 100,000
" " " " effluent "	0·46 part " "
Reduction in oxygen absorbed (no gas liquor present)	2·62
" " " " (0·5 per cent. gas liquor present) .	8·95

Considering the above points it appears that, when the gas liquor is diluted to the proportion of 0·5 per cent., the oxidizable impurity due to it is much more easily dealt with by the bacteria bed than ordinary sewage. In fact on the basis of the oxygen absorbed in 4 hours' test the " facility of treatment " of the gas liquor is 2·4 times greater than that of the sewage.

In view of the satisfactory results obtained the running of the spent liquor into the sewers was continued, the volume of spent liquor admitted to the sewers never ex-

ceeding 0·5 per cent. of the normal dry weather flow. After two years' working under these conditions further samples were taken during the dry period of September, 1929, and the following results were obtained :—

Description.	Suspended Solids.	Free and Saline Ammonia.	Albuminoid Ammonia.	Chlorine as Chlorides.	Oxidized Nitrogen.	Oxygen Absorbed. in 4 Hours. 80° F. (Unsettled).
Crude sewage .	30·0	6·18	1·12	18·2	*nil*	16·4
Settling tank effluent . .	3·50	7·33	0·71	19·6	*nil*	10·5
Final effluent .	0·50	0·93	0·17	18·0	5·0	1·56

Allowing for the dry weather period, the results are in agreement with previous observations. The analysis of the tank effluent indicates effective sedimentation and possibly some septic action. The oxidation of the sewage is satisfactory as indicated by the high oxidized nitrogen figure and the sharp fall in alkalinity. The final effluent is stable on incubation, and may be considered a very satisfactory effluent.

The conclusions are that spent gas liquor, if admitted to the sewers continuously in proportions up to 0·5 per cent. of the dry weather flow, can be satisfactorily purified at the sewage works without detriment to the beds, and that a satisfactory effluent can be maintained after continued working.

An agreement has subsequently been drawn up between the Cheltenham Gas Light and Coke Company and the Cheltenham Corporation permitting the admission of spent liquor to the sewers subject to the conditions specified.

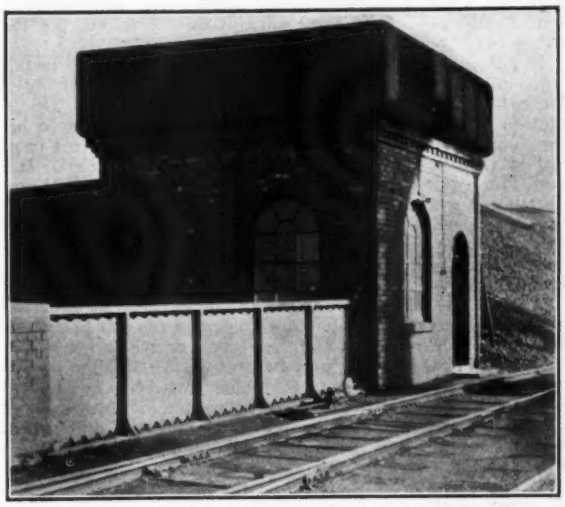
The PRESIDENT, prior to the presentation of the report for discussion, said: The conditions which govern the deposition of tar and liquid in gas-works practice as affecting the obnoxious constituents of effluent liquor are further examined in the Third Report of the Liquor Effluents Sub-Committee. Previous work indicated that a more complete separation of tar and liquor above the dew-point of water might reduce the colour-producing bodies in the liquor (higher tar acids). Experiments have been carried out with a Lodge-Cottrell tar fog extractor; and these opinions have been justified. From the point of view of "reduction in the oxygen-absorption bodies," the position has not been materially altered by the installation of the Lodge-Cottrell tar fog extractor, which admittedly is a wonderfully efficient piece of apparatus, but rather costly to run (0·15d. per 1000 c.ft.). An important point which must not be lost sight of is: What will the effects of complete tar removal from the hot gas have on the workings of the condensing plant, with special reference to the gas from horizontal retorts? The analogy is provided by the trouble from naphthalene stoppages experienced after the saturator in the direct recovery of ammonia process; here, similarly, the gas is cooled in the absence of tar fog. The removal of tar fog is desirable, but it is important that the temperature at which it is eliminated should be decided after consideration; and I suggest that below, but as near as possible, the dew-point of naphthalene would prove advantageous. In gas liquor, thiosulphates and thiocyanates are both objectionable from the disposal of effluents viewpoint, and the report gives statistics showing the reduction of these bodies by the exclusion of air from the gaseous products of carbonization; dropping the temperature of the liquor in storage; and cutting-down the circulation of liquor on the scrubbers, &c. With regard to thiocyanates, the quantity in the liquor is a measure of the removal of cyanogen from the gas—a very desirable object. It is shown that the cyanogen compounds in the gas are increased when thiocyanate is reduced in the liquor, the onus of removal being placed on the purifiers. Assuming that the purifiers are able to remove the cyanogen completely, this is only done at the expense of a reduction of oxide available for the sulphur removal. Ferrocyanide becomes an inert as far as purification and revivification are concerned. Except where it is especially intended to recover the "blue" in the oxide, it would be wise to take this into account, and balance it against the benefits which are obtained by only a partial reduction of thiocyanate in the liquor.

MR. BOTLEY'S INTRODUCTION.

Mr. C. F. BOTLEY (Chairman of the Committee): The Third Report of the Liquor Effluents Research Sub-Committee was brought to your attention last June; but there is another (the Fourth) Report dealing with various matters. In connection with the Third Report, I should like to draw attention to the diagrams, drawings, and photographs of that very fine installation of bacteria beds at Coventry, which are published through the kindness of Mr. P. N. Langford, of Coventry, who is a member of the Effluents Sub-Committee. I am sorry that the Superintendent of the Chemical Works at Coventry is unable to be here, because he takes a great interest in the installation at Coventry, and we are greatly indebted to him. I had hoped that the Chairmen of the Committees at Coventry and Hinckley would have been here to-day, but, unfortunately, they were unable to come. I should like to thank those gentlemen for the way in which they encourage their Committees to deal with the effluents problem.

In the Fourth Report we have brought the available matter up-to-date. We have by our researches shown the way to reduce the higher tar acids, but we have been led, rather unexpectedly I think, to an increase of phenols. It looks as though it is becoming a question of phenol recovery, and it is because of this that we have been giving some attention to phenol recovery. In dealing with ammonia liquor, we can concentrate on the works, as shown in Mr. Hollings' paper, up to a strength of (say) 18 oz., but there is also the concentration of the plant, so that, if it were economically possible, we could send the liquor to large centres where the final treatment would not be so difficult as it would be if we attempted it on a small scale. I want you to bear that aspect in mind. If we can solve the phenol question, we have still the higher tar acids to consider.

With regard to the summary (prepared by Dr. Monkhouse) of the purification work at Cheltenham, the value of it is that it shows what can actually be done at the present time in the disposal of a properly controlled effluent to the sewage system. It is important because some of our friends connected with sewage works seem to think that this effluent is a great burden. Though we must be sympathetic with them, I think we can say



Storage Tank at the Cheltenham Gas-Works for waste liquor from the Sulphate of Ammonia Plant. The liquor from this tank, Mr. L. E. Twycross, the Engineer to the Cheltenham Company, informs us, passes to the Town Sewer through a Recorder made by the Palatine Engineering Company, Ltd., of Bootle, Lancs. The flow is continuous; being ½ p.ct. of the dry-weather flow of town sewage.

definitely that, with proper control, the effluent can be admitted to the sewage system of a town without too great detriment to the sewage works.

Discussion.

Mr. L. H. SENSICLE: The effluent problem is intimately connected with the question of recovery methods. These have been the subject of a very useful report by Dr. Parker, and I am substantially in agreement with the conclusions of that report. There are, however, one or two matters I should like to criticize.

Dr. Parker seemed to over-emphasize the power costs of the direct method of recovery. It is true that the handling of hot gas involves the consumption of more power than if the gas is cool, as in the indirect method. But the statement that the consumption of power is four times as much as in the latter case is surely an exaggeration. Assuming that coal containing 3 p.ct. of adhering moisture, and yielding 6 p.ct. of water by destructive decomposition—*i.e.*, yielding 9 p.ct. of water on carbonization—were used, the volume of gas *plus* water vapour at 80° C. would be only 1·6 times the volume saturated at 15° C. (or 60° Fahr.). Thus the power for driving the exhauster would be only 1·6 times that for an exhauster used in the indirect process. As regards the tar extractor for the direct process, it is necessary to neglect the power for the liquor sprays in making comparisons, because the power for circulating and transporting liquor at the scrubbers in the indirect process has not been considered.

Dr. Parker has made calculations for the possible power consumption per ton of sulphate of ammonia, and it would appear

that the basic figures are wrong. Assume a large plant making 1 ton of sulphate per hour: The cool gas corresponding to this make is 1,200,000 c.ft.; and assuming it to be handled by an exhauster in the indirect process, which raises the pressure to 30 in. W.G., it can be calculated that the horse-power in the gas is 108 after the exhauster. Allowing 50 p.ct. for the mechanical efficiency of the exhauster, the power required for the exhauster amounts to 216 H.P. That is to say, the consumption of energy for exhausters per ton of sulphate of ammonia is 216 H.P.-hours. Multiplying by 1·6, the figure of 345·6 H.P.-hours is obtained for the corresponding energy in the direct process. The difference—129·6 H.P.-hours—is much smaller than the figure of 500 given by Dr. Parker. Further, the cost of this power should not be more than 0·3d. per H.P.-hour in an efficient works, and so the difference in cost of power for exhausting should be 3s. 3d.

It is said in the report that it is not possible to predict whether the capital and maintenance costs for the direct process would be greater or less than those of the indirect process; but it is only necessary to apply to plant constructors specializing in both forms of recovery plant to discover that the capital cost of the complete plant for direct recovery is considerably less than the cost of equal capacity indirect recovery plant. The maintenance costs are also definitely lower.

Reference to Mr. Hollings' report is instructive as regards the costs which are likely to be largely eliminated by choice of direct recovery in preference to the indirect process. For example, Mr. Hollings estimates the interest and depreciation in respect of ammonia scrubbers alone to amount to 10s. per ton of sulphate. Further, in respect of liquor, he gives costs for transport and pumping, storage, water and steam at gas-works, and steam for distillation at a total of £1 7s. 11d. per 1000 gallons. Thus, assuming 8½-oz. liquor—*i.e.*, 3000 gallons per ton of sulphate—these costs amount to £4 3s. 9d. per ton of sulphate.

Dr. Parker made the assertion that a saturator of usual design in direct recovery cannot be operated successfully with large fluctuations in the rates of gas production. This contention is a concession to the early failures experienced in the gas industry when a process purporting to be a direct process, but in reality less than one-quarter direct, was tried. It is a fact that coke oven plants have been worked at half-normal output for weeks on end without disorganization of the working of their direct recovery saturators. As mentioned by Dr. Parker, there have been designs of saturator proposed which are specially intended to deal with large fluctuations of gas throughput.

Though the sulphate made in the direct process has a somewhat small crystal, this has not prevented the salt being sold at the same market prices as other types, and it is usual for the full allowances for dry and neutral friable quality to be obtained. It is noteworthy that the North of England Gas Managers' Association in a recent visit to a coke oven plant passed through the direct sulphate plant house and salt store without many of the members realizing that the sulphate was made by the direct process.

It is a mistake to assume that tar is trapped in the sulphate of ammonia in the direct process. This is not the case, because the tar, if any, passing as fog to the saturator is lighter than the acid liquor, and floats as a scum which is readily skimmed off.

Dr. Parker's suggestion that the direct process might be modified by preventing crystallization of the sulphate and removing a nearly saturated solution for separate crystallization appears well worth consideration, but it would seem to be a procedure likely to detract slightly from the advantage of low costs associated with the direct process.

From the point of view of the effluents question, the advantage of the direct process is now well known. The effluent from a horizontal retort installation would be only about one-fifth the bulk of that common at present, while the main deleterious constituents of that effluent—viz., monohydric phenols—are extractable with profit by processes such as are described in Dr. Monkhouse's report.

Since the direct and semi-direct processes of ammonia recovery are not hypothetical methods of dubious practical success, but are widely adopted operations in the bye-product coking industry, it would be unfortunate if the Institution condemned them before they have actually been tried out at gas-works using the present common types of carbonizing plant.

Work at Cheltenham.

Mr. F. R. O'Shaughnessy (who has been connected with the work at Cheltenham) said: I think the first line of attack of the effluent problem must be within the industries producing the effluents; and experience indicates that, when the attention of manufacturers has been drawn to the difficulties experienced outside by the sewage people, often modification within the manufacturers' works is more or less easy. It is very gratifying to know that in your industry you are very active in this direction, with a view to relieving the burden which is imposed on the sewage people. I am interested in the biological effect. I think there is no question that the method of disposal adopted at Cheltenham has the advantage of the others mentioned, on the score of cost. Mr. J. S. Pickering (the Borough Engineer at Cheltenham) asked me to examine the effluent after two years' steady addition of the gas liquor to the Cheltenham sewage—and I understand that the average proportion over twelve months is something like 0·3 p.ct. by volume of the sewage flow. The results I obtained after two years' operation under those conditions rather lead me to suspect that the gas liquor actually stimulates the biological activity in the bed to a small extent. We were unable to carry out exhaustive experiments, but I supplemented my investigations by laboratory tests—which are mentioned in the report—and they indicate that when the 0·5 p.ct. limit is passed, the difficulty introduced by the gas liquor does increase very rapidly, and by the time the flow is increased to 1 p.ct. it is beginning to have quite a detrimental effect.

I have suggested several times to Dr. Monkhouse that possibly there is some other method of assessing the value or strength of the gas liquor than the four hours' oxygen-absorbed test, because in my opinion this method is very unsatisfactory. It would be far more satisfactory to adopt the "B.O.D." (biochemical oxygen demand) method. If this figure were determined under strictly specified conditions, we should get a standard which would be much more satisfactory than the four-hour permanganate figure, and which would not suffer from the disadvantage of being extremely arbitrary. When we speak of the effect of the addition of gas liquor, we have regard merely to percentage volume; but I would point out that since the chemists first investigated this matter, some 25 years ago, the strength of gas liquor has increased substantially, on the basis of the four-hours' oxygen absorption, and also on the basis of the absolute constituents present. The Royal Commission came to the conclusion that one might add gas liquor from a gas-works to the extent of 2 p.ct. of the sewage flow without expecting any trouble. This held pretty well on their results—and they examined liquors varying in concentration from 60 to 600 or 700 parts per 100,000, which indicates that even at that time there was an enormous variation in the strengths of these liquors. Since that time the strength of liquors has at least doubled, and it is no longer possible, therefore, to accept that figure of 2 p.ct. My own opinion is that 0·5 p.ct. does not give rise to any serious problems if the material is added in a properly controlled manner—and this is most important. But I would suggest, especially now that it seems likely you will simplify chemically the discharge from the gas-works, that possibly you may be able to adopt a basis more satisfactory than that of the volume discharged or the four hours' permanganate figure.

Recovery of Phenol and Higher Tar Acids.

Mr. D. W. Parkes (Messrs. Robinson Bros., West Bromwich): The points which interest me particularly are those concerning the recovery of phenol and the recovery of what you call the higher tar acids—which latter you have not recovered in your experiments, but which we have recovered actually as crude catechol. I am interested to notice that in Germany they are doing something with carbon. I do not know if there is any further information forthcoming, but, as far as I can gather from this report, they are recovering the phenols from the carbon by washing with benzole. It would be interesting to know to what degree they dry the carbon before they extract the benzole. We tried various solvents before we tried steaming our tar acids from the carbon, but could not get any satisfactory results on the moist carbon. In order to get the carbon really dry it is necessary to raise the temperature to something like 400° C., and by that time you have got the majority of your phenols over; but no doubt they have found some method of getting the tar acids out, and it would be very interesting to know what it is. It has been said that an objection to the process for eliminating tar acids from liquor is that the tar acids are recovered in the form of a very dilute solution. We did recover them in that form, and sometimes we got them back in a more dilute form than when they were in the original liquor, but in the end we obtained 50 or 60 p.ct. of them as liquid and separable tar acids, by adjusting the method of distillation.

It might be of interest to examine the requirements for dealing with the Foleshill liquor by means of the carbon plant. I work it out that the quantity would be about 1200 gallons per hour; and to deal with this by activated carbon we should require about 1000 lbs. of carbon in circuit. It is also interesting to compare the space occupied by the carbon plant with that occupied by the filter beds. The filter beds cover, roughly, 600,000 sq. ft. of surface. A carbon plant would be useful, I imagine, in a crowded town area, where there is not the space available for providing enormous beds.

Value of Higher Tar Acids.

I was very interested in the experiments made by Dr. Monkhouse with a view to reducing the higher tar acids, because we are trying to do just the opposite. We are endeavouring to find liquors now with higher tar acids in them; and, in fact, during the last six or seven months we have recovered—and have recovered at an extraordinarily low price as compared with the cost of catechol now—between 1 and 2 cwt. of crude catechol from liquors, and have despatched it to manufacturers who are investigating its use for fine chemical manufacture. It will be rather a blow to us, there-

fore, if we cannot get liquors containing higher tar acids. No doubt Dr. Monkhouse will devise a means of recovering them in the form of a liquor, and we shall get them in that way—*i.e.*, they will not go into the main body of the liquor.

I do not know whether I misunderstood the remarks of Dr. Monkhouse with regard to the tar extractor, but he said, I believe, that the whole of the ammonium chloride went into the tar. If that is so, I am sure the tar distillers will be taking notice. We have had a little experience with large quantities of ammonium chloride in the tar, due to some modern installations, and they have given enormous trouble, which at present we are endeavouring to overcome.

A Prediction Verified.

Dr. S. PEXTON (Gas Light and Coke Company): I have been particularly interested in the results of the investigations at Hinckley, and one particular feature of these results is the very high yield of tar per ton of coal. This suggests that the distillation of the coal is taking place in the upper part of the retort at a comparatively low temperature. Washed screened coal was used, and it seems very likely that the tar which was produced under these conditions resembled the tars made in low-temperature carbonization units rather than those normally manufactured in vertical retorts employing unscreened coals. This undoubtedly made the problem of producing a colourless ammoniacal liquor, reasonably free from higher tar acids, a particularly difficult one. It has, however, been shown that, by precipitating the tar electrostatically from the gas at a temperature above the dew-point, the liquor subsequently produced is practically free from the colour-forming constituents. At the same time, this had been done at the expense of a considerable increase in the monohydric phenol content of the liquor—an effect which was predicted in the discussion on liquor effluents at the Carbonization Conference in Birmingham in February, 1928. [See "JOURNAL" Carbonization Conference Supplement; March 7, 1928, p. 127.]

The question now arises, What is the correct procedure in the following case? Unscreened Durham coal was carbonized in vertical retorts with a yield of 28·5 gallons of ammoniacal liquor (12-oz. strength) and a yield of approximately 11 gallons of tar per ton of coal respectively. The liquor had the following analysis:

—	Equivalent Lbs. of Oxygen Absorbed per 100 Tons of Coal Carbonized.	
Higher tar acids—		
G. of oxygen absorbed per 100,000 c.c. of liquor	24	7·1
Oxygen absorbed ($KMnO_4$, 4 hrs. at 27° C.)—		
Due to Thiocyanate	90*	26·7*
Thiosulphate	28	8·1
Phenol	407	120·4
By difference	202	59·8
	727	215·0

* 60 P.Ct. from purifiers.

These results approximate to those obtained in horizontal retorts. A further comparison which might be made is that considerable quantities of naphthalene were produced under these conditions. It is almost certain that, if the tar had been precipitated from the gas above the dew-point, naphthalene stoppages would have occurred in the condensers. Apparently this difficulty did not exist at Hinckley when using the tar precipitator, because of the absence of naphthalene in the tar and the gas. In addition, it is the experience of some engineers when carbonizing unscreened Durham coal in vertical retorts that it is necessary to circulate tar rather than liquor through the gas collecting mains in the retort house, in order to prevent deposits of pitch. In these circumstances the tar becomes contaminated with ammonium chloride, and it is essential to allow contact between the tar and liquor at a later stage in order to dissolve the ammonium chloride.

Thus, while the removal of tar above the dew-point may help to solve the difficulties of effluent disposal in certain cases where the polyhydric phenols predominate and where naphthalene is practically absent, yet there are other cases of vertical retorts in which it cannot be anticipated that the method would be advantageous or practicable. It is certainly very doubtful whether the method would be practicable or advantageous with horizontal retorts.

Turning to the Fourth Report upon Effluents, I should like to ask the authors whether any experiments have been made to ascertain whether the benzole extraction processes will remove the polyhydric phenols from liquors, such as those produced at Hinckley without tar precipitation, to a sufficient degree to render them colourless on exposure to air.

I would like to impress upon the members the fact that both the Ammonia Report and the Effluents Report are of an interim nature, and we are continuing our labours in various directions.

Reply of Dr. Monkhouse.

Dr. MONKHOUSE, replying to the discussion, said: With regard to direct and semi-direct recovery, we have had samples from a semi-direct recovery plant at a gas-works, and the very low thiocyanate and thiosulphate content of the liquor is very noticeable. Mr. O'Shaughnessy has mentioned the 0·5 p.ct. limit, and it is an interesting fact that, if you compare the average flow of gas liquor with the average dry-weather flow of sewage over the year in the same area, the former works out at approximately 0·5 p.ct. of the latter. It is less at Cheltenham, however, because they use rather more water there than at other places; factors such as this have their influence.

I am sorry I cannot give Mr. Parkes any more particulars with regard to the German process, except that I am told it is being worked out on a medium-scale plant, and the people in Germany are putting up a large-scale plant which they hope to have in operation next month. As to his desire for more of the higher tar acids in the liquor, would he be willing to pay gas-works a higher price for such liquor, and is his process practicable, and carried out on a sufficient scale for application in the ordinary gas-works? I agree with his statement as to the large area covered by the Foleshill bacteria beds; they occupy about an acre.

I was very interested in Dr. Pexton's remarks. I have examined a number of samples of vertical retort liquor, and his is one of the best I have ever had. I should say, as he has done, that it is very nearly a horizontal retort liquor. The high yield at Hinckley is due to the conditions Dr. Pexton mentioned. They are using there washed screened coals, and the temperatures are not high, the combustion chamber temperature being about 1350° C. In the old plant, where it is necessary to have rather a higher pull, we do not get quite so high a yield as 15 gallons per ton; also, there is no trace of naphthalene. With regard to the ammonium chloride, I did say, as Mr. Parkes has pointed out, that it is brought down with the tar, in the spray method of circulation. This, of course, is a method by which you can bring out the tar from the gas, and at the same time remove ammonium chloride from the tar, by the circulating liquor. Of course, you have to remove the fixed liquor from time to time, to recover the ammonium chloride. We are carrying out experiments at Hinckley on benzole extraction from vertical retort liquor. We had a laboratory apparatus for making continuous flow tests with vertical retort liquor, and hope to be able to obtain data which will help us in connection with this method of recovery for use with vertical retort ammonia liquors.

Vote of Thanks to the Effluents Sub-Committee.

Mr. DOUGLAS H. HELPS (Reading): I have much pleasure in proposing a hearty vote of thanks to the Effluents Sub-Committee and to Dr. Monkhouse and his staff for the great work they have done. Even if we were now getting the same price for our sulphate of ammonia as we were obtaining when I first went to a gas-works—between £20 and £21 per ton—the work done by the Committee would have been justified; but now that the price has fallen to between £7 and £8, this work is still more important. Again, it is valuable in consequence of the difficulties which have arisen in towns where delicate new systems for the treatment of sewage have been adopted; in my opinion, some of the systems are too delicate. I remember a report which Dr. Woelcker was asked to make to the Croydon Gas Company, 35 or 40 years ago, in connection with difficulties which had arisen on the sewage farm there; and his report, in my recollection, was that the experiments he had carried out showed that the effluent from the sulphate works was actually beneficial to the sewage plant. Systems of sewage disposal have been altered since then, of course, as also have our methods of manufacturing gas. The whole position has been rendered much more difficult.

Lieut.-Col. W. M. CARR (Stretford): I have very much pleasure in seconding this vote of thanks to Mr. Botley and his Committee, and to the Research Chemists, who have put before us such excellent reports; and in doing so I should like to place on record my testimony to the value that the First and Second Reports of the Ammonia Sub-Committee have been to me personally in my own works, in that, because of those reports, I have been able to adopt something which will, I am sure, effect a substantial financial saving. The difference between being able to produce a 12-oz. and an 8-oz. liquor is a substantial matter to my gas undertaking. At times we may be inclined to ask ourselves what we get out of these research reports, but I personally believe that we get 100 p.ct. value if we make use of the wonderful work which is being carried out.

The vote of thanks was carried with acclamation.

Mr. BOTLEY, responding, said: The best reward you can give us is that which Mr. Carr has indicated—*i.e.*, the knowledge that you are making use of the information placed at your disposal. With regard to effluents, it is part of our work, while we are seeking a better solution, to assist any undertakings which may be in trouble; and we have had some measure of success in this. The Research Staff do all the work which is put before you, of course; I am simply the

mouthpiece for my practical colleagues. Prof. Cobb is always ready to advise when the Committee is not sitting, and he is always most helpful in the way he deals with anything put before him.

Dr. Parker's Paper.

The President: Dr. Parker has been kind enough to suggest that he should give us a brief summary of his paper. He asks that you should communicate in writing any criticisms you may have to make upon it; and I will undertake to set apart a short session at our annual meeting in Leeds next summer—if we cannot have a meeting in the meantime—in order that he may reply to them.

Dr. Parker introduced his paper.

Vote of Thanks to the Ammonia Sub-Committee and Research Staff.

Mr. John Terrace: It is my pleasing duty to propose a vote of thanks to the Chairman and members of the Ammonia Sub-Committee, and to the members of the Research Staff. The selection of that Committee has been largely in the hands of the Chairman; and I think we ought to congratulate Mr. Botley upon his discrimination in gathering around him such a body of eminent men able to carry out the work so satisfactorily. I am sure that the whole of the members of the Institution, and especially those who have listened with such great interest during the last two days to the various reports presented, will do all they possibly can to help them.

The President: I should like to second this vote of thanks, and to endorse what Mr. Terrace has said. The interest which has been displayed to-day reflects great credit upon the Chairman and his fellow-members of the Committee, and upon the Research Staff.

The vote of thanks was carried with acclamation.

Mr. Botley, after again expressing thanks, asked Prof. Cobb to reply on behalf of the workers of the Committee.

Prof. Cobb: I should like to associate myself with the Chairman's remarks concerning the members of the Committees, and particularly of the Ammonia Sub-Committee. I have had experience of a large number of technical committees, but I do not think I have ever known one which better deserves the name of a working committee than does the Ammonia Sub-Committee. We knew that the subject was too wide to be surveyed by the Secretary or the Chairman of the Committee, or by a research chemist. The constitution of the Committee was such that we were able to divide the subject-matter into various groups; and for each of these groups some specially competent person made himself responsible. That is the reason why this series of sectional reports has been put forward. They are discussed by the Committee before presentation to the Institution, which is an excellent working arrangement.

A vote of thanks to the Institution of Electrical Engineers was proposed by the President, and seconded by Mr. Botley.

Vote of Thanks to the President.

Mr. P. N. Langford: I am sure you will agree that we cannot conclude this memorable conference without passing a hearty vote of thanks to our President for the able and efficient manner in which he has presided over our deliberations during the past two days. This is not the time or the place to extol his virtues, but, speaking for those members of the Institution who live in the Provinces, I must say that we are very much inspired by his kindly and keen interest in the work of the District Associations, and we appreciate the fact that he devotes such a great deal of work and time to the welfare of the industry as a whole.

Mr. A. G. Gregory (Harwich) seconded the vote.

The reply of the President brought the meeting to a close.

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